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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute was held at 26 Portland Place, London, W.1, on 8 October 1952, Mr R. B. Southall, vice-president, in the Chair.

THE CHAIRMAN said: Mr Joyce, who is to present a paper this evening started his career with a long period of practical experience in the steel industry. After the first world war his practical work was accompanied by studies at Sheffield University, where he obtained a diploma in civil engineering. He has had extensive experience since that time in the petroleum industry with the Shell Group, with a long period at Fulham and more recently at the Thornton Research Centre.

During the second world war Mr Joyce was making contributions to the development of the Whittle jet engine, first with Power Jets Ltd, and later with the Ministry of Aircraft Production and the Ministry of Supply.

The following paper was then presented by J. R. Joyce:

METHODS OF ATOMIZING LIQUID FUEL

By J. R. JOYCE *

SUMMARY

After reference to the purpose and significance of liquid fuel atomization, and a detailed consideration of the mechanism and physical extent of the process, a general description is given of the main types of practical atomizer or oil burner, with comments on the operational requirements and characteristic features of each.

Considerations affecting the choice of atomizers are reviewed, and a brief discussion of the cost of atomization follows.

The desirable features to be looked for in a good atomizer are set out, followed by a reference to requirements in testing, including a consideration of specialized tests to examine spray pattern symmetry, and also spray particle size distribution.

The main physical factors in burners which affect the quality of atomization are mentioned. The only fuel factor regarded as significant in this connexion is viscosity, and the advantage of appropriate fuel pre-heating in the case of heavy oils is duly noted.

The fact that good atomization is not the only factor in efficient fuel burning is stressed, and the parallel need for a balanced and properly directed air supply is emphasized.

MEANING AND PURPOSE OF "ATOMIZATION"

FUELS of all kinds, solid, liquid, and gaseous, are virtually worthless alone. All demand alliance with a certain other element before they can be induced to release their rich store of heat energy. This element is oxygen, and nature provides an inexhaustible supply of it in the atmospheric air.

In alliance with oxygen, fuels will burn, releasing their potent energy store to be exploited for various purposes. The union of a fuel with oxygen may be very haphazard, or it may be organized and systematic.

* Thornton Research Centre, The Shell Petroleum Co. Ltd.

In the former case the fuel energy is expended wastefully; in the latter case with due economy and efficiency, in degree dependent upon the care with which the alliance between the two is promoted and fostered.

" Atomization " is the established term used to describe the organized preparation of liquid fuels for efficient burning. It is the equivalent of " pulverization " in the case of coal. In atomizing a liquid fuel force is applied to it in an organized way so that the bulk liquid is converted into a spray composed of minute droplets as small in general size as can be achieved by practical means.

This process of atomization, or spraying, is essentially the preparation of the liquid fuel for its most efficient and intimate union with oxygen, so that its store of heat energy may be most effectively released with the minimum of waste. Of equal importance to this proper preparation of the liquid by atomization is the proper introduction of the essential oxygen available in the air, but this aspect of the matter is just outside the scope of the present paper, which is concerned with the fuel side of the partnership.

In atomizing a liquid fuel the final purpose is always the same: to produce surface area. There is no known mechanical process by which oxygen can be infused into the fuel, or vice versa. The best that can be done is to produce increased surface area, so that when the fuel and air are mixed, the latter finds physical contact with the former by the maximum degree of envelopment or surface contact.

The Extent of Atomization

A simple example will serve to illustrate how " atomization " expands surface area.

A cubic centimetre of liquid fuel would, under the action of surface tension, assume the form of a sphere approx 1·24 cm in diameter, and its surface area (in contact with the air) would be $\pi d^2 = 4{\cdot}83$ sq. cm. Assuming that by some means this sphere is divided into one million equal-sized small spheres, each having a volume of 10^{-6} cc, each would have a diameter of 0·0124 cm, and in the aggregate the total surface area of all of them together would be 483 sq. cm. or one hundred times that of the original single sphere.

Atomization of liquid fuels by various types of atomizers or burners breaks up each cubic centimetre of the fuel much more finely than this, and in a random array of sizes, so that after the atomization process the amount of fuel surface exposed to air envelopment may range up to 1500 sq. cm. per cc or even higher, the droplets in the spray ranging in size from " fines " in the 1-μ (0·0001-cm) region up to coarser droplets in the 500-μ (0·05-cm) region and each cubic centimetre of fuel being divided into tens of millions of droplets.

In the actual process of atomization force is applied to the liquid fuel in such a way as to set it in motion and generally to lead to the formation of an attenuated liquid film which, under the further action of applied force, breaks up into short ligaments or threads of random size.

Principally due to the action of surface tension, these ligaments subdivide into several parts, forming main and satellite droplets. Thus, the ensuing spray inevitably consists of droplets covering a very wide spectrum of sizes indeed.

Means of Effecting Atomization

Atomizers, or burners as they are widely called, are to be found in a great variety of forms, but may be classified in three main groups.

Group 1—*Two-fluid Atomizers*

In this group are to be found what are sometimes called " two-fluid " atomizers, because they employ a second fluid or agent—either air or steam —to promote atomization. Subdivision into sub-categories is desirable because of the variety of types, and because some of them are designed to use air exclusively as the second fluid, whereas others may use air or steam according to circumstances.

Group 1 (a) *L.P.A. Atomizers*

Fig 1 shows a well-known example of this type, generally called a low pressure air (L.P.A.) atomizer. A suitable fan supplies air at a moderate delivery pressure from 10 up to 25 inches water gauge. Owing to the low

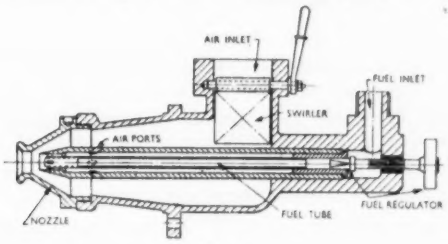

Fig 1

LOW PRESSURE AIR (L.P.A.) ATOMIZER (WALLSEND)

pressure level it is usual to pass at least 25 per cent of the combustion air through the burner for atomization purposes. Sometimes, for special reasons, the full stoichiometric quantity may be passed through the burner. Because of their flexibility and their ease of control, burners of this type find a wide field of application in small and medium size industrial furnaces.

In the example illustrated the air can be given some measure of swirl or rotary motion in its passage towards the burner nose. A small proportion of the air is taken through the oblique air ports, serving mainly to even out the flow of fuel emerging from the end of the central fuel tube. The main air supply picks up this primary oil–air mixture in the convergent nose, and promotes ligament and droplet formation by its high velocity at this point. This type is exclusively an air atomizer. The fuel may be fed to it by gravity from a service tank.

Group 1 (b) *M.P.A. Atomizers*

Figs 2 (*a*) and (*b*) show two forms of medium pressure air (M.P.A.) atomizers, the first an " external mixer " and the second an " internal mixer." The atomizing air, at pressures ranging from 3 to 10 p.s.i., is admitted to the outer annular space surrounding the central oil feed tube. Alternatively, dry steam at a pressure of about 10 p.s.i. may be used. Usually from 3 to 6 per cent of stoichiometric air is used for atomization

purposes, representing from 6 to 12 cu. ft. of free air per lb of liquid fuel atomized. The air or steam may be given a swirling motion at or near the nose, where, at very high velocity, it entrains the metered oil supply and shatters it. Some burners of this type can be fed with fuel oil by gravity,

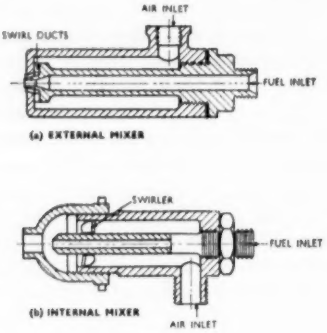

FIG 2

MEDIUM PRESSURE AIR (M.P.A.) ATOMIZERS

but it is generally better to provide for positively metered feed by low pressure pump.

Group 1 (c) *High Pressure Air or Steam Atomizers*

High pressure air (H.P.A.) or steam atomizers are well exemplified in Fig 3. Ordinarily, air or steam at a pressure of 50 p.s.i. or higher is employed, and it is rare for more than $2\frac{1}{2}$ per cent of stoichiometric air to be

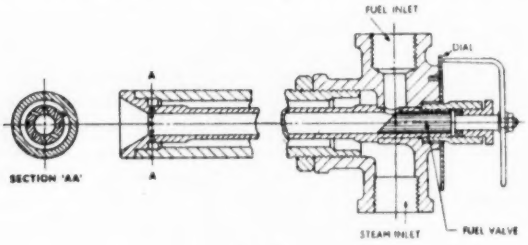

FIG 3

STEAM OR HIGH PRESSURE AIR (H.P.A.) ATOMIZER (CLYDE)

used, on the score of economy. With steam it would be unusual to use more than 0·4 lb/lb of fuel atomized, for a similar reason. It may be noted that 0·4 lb of steam represents approximately 3 per cent of the weight of steam that would be raised in a boiler fired by the burner.

Group 1 (d) *The Scent-spray Atomizer*

The " scent-spray " atomizer (Fig 4) is a further example of an external mixing air or steam atomizer of moderate or high pressure type. The jet

of steam or air, emerging at high velocity across the end of the fuel tube, shears off the liquid into fine shreds, and these break into droplets. This

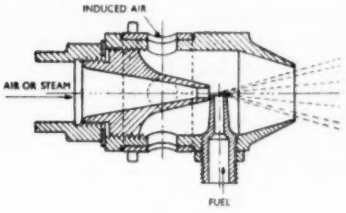

FIG 4

"SCENT-SPRAY" AIR OR STEAM ATOMIZER

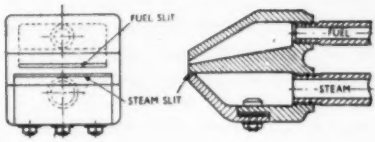

FIG 5

DROOLING OR WEIR TYPE ATOMIZER

type is not very widely employed, and may require slightly higher proportions of air or steam than indicated in the previous section.

Group 1 (e) *The Weir Type Atomizer*

The drooling or weir type atomizer shown in Fig 5 is yet another external mixing type of two fluid atomizer. In this case the liquid fuel emerging from the upper slit-like orifice cascades over into the very high velocity steam or air blast emerging from the wider slit-like orifice situated just below, and is torn to shreds instantaneously, resulting in a very well atomized spray. This particular type of burner has long enjoyed a favoured place in the oil-firing of locomotive boilers and, properly installed, will handle up to 2500 lb of fuel per hour in a locomotive boiler firebox, using steam at pressures reduced to 50 p.s.i.

Group 2—*Mechanical* (*Rotary*) *Atomizers*

Figs 6 (*a*) and (*b*) illustrate the operating end of two of these atomizers. The liquid fuel is metered at the desired rate into the smaller end of a cup-

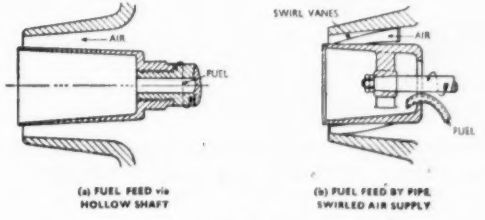

FIG 6

ROTATING CUP ATOMIZERS

like member which tapers more or less gradually to a maximum diameter at the lip or discharge end. The cup is rotated at high speed (from 2850 up to 8550 r.p.m.), and the fuel spreads as a film over its surface, moving

forwards towards the lip. Here it is flung off by centrifugal force and is caught up in the high velocity air blast emerging from the annulus surrounding the cup. In so far as the atomization produced by the cup alone is relatively coarse, and the air blast serves as a second stage atomizing medium as well as a spray director—this burner could be included in the " two-fluid " atomizer category. The spinning cup can be arranged with its axis horizontal or vertical, and may be driven by mechanical or electrical means, or by air acting on suitably disposed turbine vanes on the outside

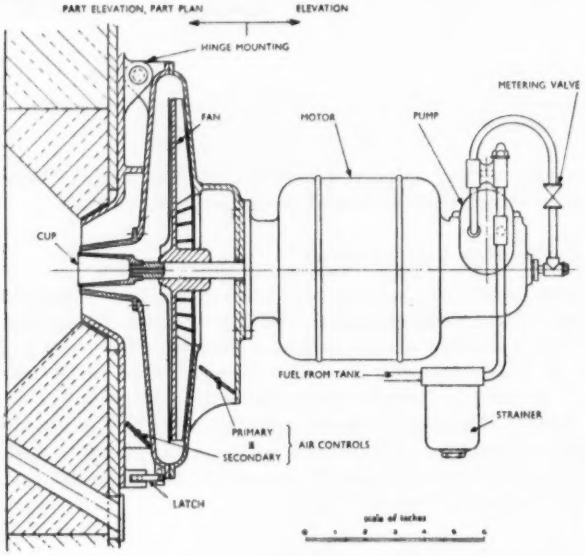

FIG 7

MOTOR DRIVEN ROTARY CUP BURNER

of the cup itself, which is then carried in the mouth of the air supply tube in suitable bearings.

A complete burner of rotary cup type is illustrated in Fig 7.

Group 3 *Pressure Jet* (*Single-fluid*) *Atomizers*

In this type pressure energy in the fuel is converted into kinetic or velocity energy in the atomizer. Two main types are to be found :—

Group 3 (a)

Plain hole types, as used almost exclusively in compression-ignition engines for the purpose of intermittent fuel injection into each cylinder in turn. Commonly these types are fed with fuel at very high pressure, ranging up to 8000 p.s.i., promoting extremely fine atomization, yet providing a spray capable of penetrating into the highly compressed air-

charge in the engine cylinder. Figs 8 (*a*) and (*b*) show two typical examples.

Group 3 (b)

The centrifugal swirl types, as used almost universally under the boilers of naval and mercantile vessels, and in many land installations. With this type the fuel pressures employed are much lower, rarely exceeding 350 p.s.i. An exception to this is the aero-gas turbine, where pressures up to 1200 p.s.i. are employed for reasons associated with the wide fuel flow ranges involved in such cases. The basic principle of the centrifugal pressure jet atomizer is shown in Fig 9. The fuel under pressure is fed into the swirl chamber through two or more equal-sized tangentially disposed ports or channels. A free vortex is set up and, on the principle of the conservation of momentum, the angular velocity increases towards the axis

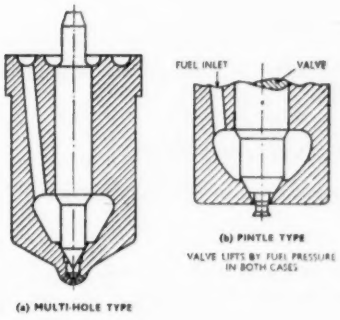

FIG 8
TYPICAL DIESEL INJECTION NOZZLES

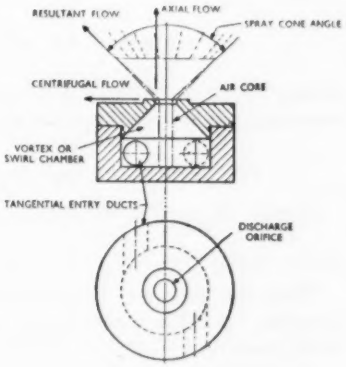

FIG 9
THE PRESSURE JET ATOMIZER

of the assembly, which has a discharge orifice for the egress of the swirling fuel. Since at the axis of the vortex where the radius is zero the angular velocity would theoretically be infinite, this impossible condition is obviated by the formation of an air-core concentric with the discharge orifice. Under conditions of stable operation at any suitable supply pressure the fuel passing out of the discharge orifice is thus in the form of a hollow tube or pipe of liquid swirling round at high speed. Leaving the orifice the centrifugal component of the forces acting on the liquid tends to make it fly outwards all round at right angles to the axis, while the axial component tends to make it flow axially forward. As a result of these applied forces, the fuel emerging takes the form of a divergent hollow conical film, which diminishes in thickness as it grows in diameter and which ruptures and breaks up into ligaments and threads at quite an early stage. The formation of droplets ensues, and the fuel is thus discharged from the atomizer as a very finely atomized divergent conical spray, quite hollow until it has travelled some distance or has been churned up by the air admixed for combustion. Fig 10 is a high-speed photograph of such a spray in the early stages of development.

As a special case of the pressure jet, the example shown in Fig 11 is of passing interest. By the injection of some fuel axially into the air core region of the vortex it is claimed that a solid cone of spray is produced, but the writer has no experience or knowledge of its use in oil firing in the U.K.

Many different forms of the swirl-type pressure jet are to be found in practice, but in essence all are fundamentally alike in exploiting a free

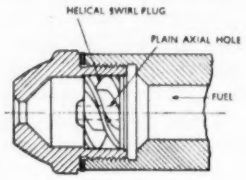

FIG 11
PRESSURE JET WITH "SOLID" SPRAY CONE

vortex developed by means of hydraulic pressure. A fairly comprehensive description of several types is available.[1]

FEATURES OF THE DIFFERENT TYPES OF ATOMIZERS

Certain features of the different types are worth brief consideration.

Steam Atomizers

These are generally the least expensive to instal and are quite simple to operate. A fairly wide output range can be obtained, from 5 to 1 on the small sizes up to 7 or 8 to 1 with those of larger capacity.

Care must be taken to use dry steam, as it is possible to extinguish the flame if wet steam or slugs of water enter the burner, particularly at low fuel rates.

It is not uncommon to find steam burners operating with a grossly excessive steam consumption, because operators often increase the steam quantity as an easy way of curing smoke. Auxiliary starting equipment is sometimes needed, as for instance in the case of a steam boiler fired by the burner.

Air Atomizers—High and Medium Pressure

These are characterized by flexibility and ease of control. Output ranges up to 5 to 1 are obtainable in the smaller, and approaching 10 to 1 in the larger sizes.

In applications where the combustion air is pre-heated by recuperators or regenerators, the fact that only some 5 per cent of the total air is required cold in the burners for atomization purposes means that some 95 per cent of the air can be highly pre-heated, leading to corresponding economy in fuel consumption.

The high pressure types necessitate quite costly compressor equipment and are somewhat noisy in operation, a factor which may be of importance in some instances.

FIG 10

PRESSURE JET ATOMIZER IN ACTION

[*To face p.* 64.

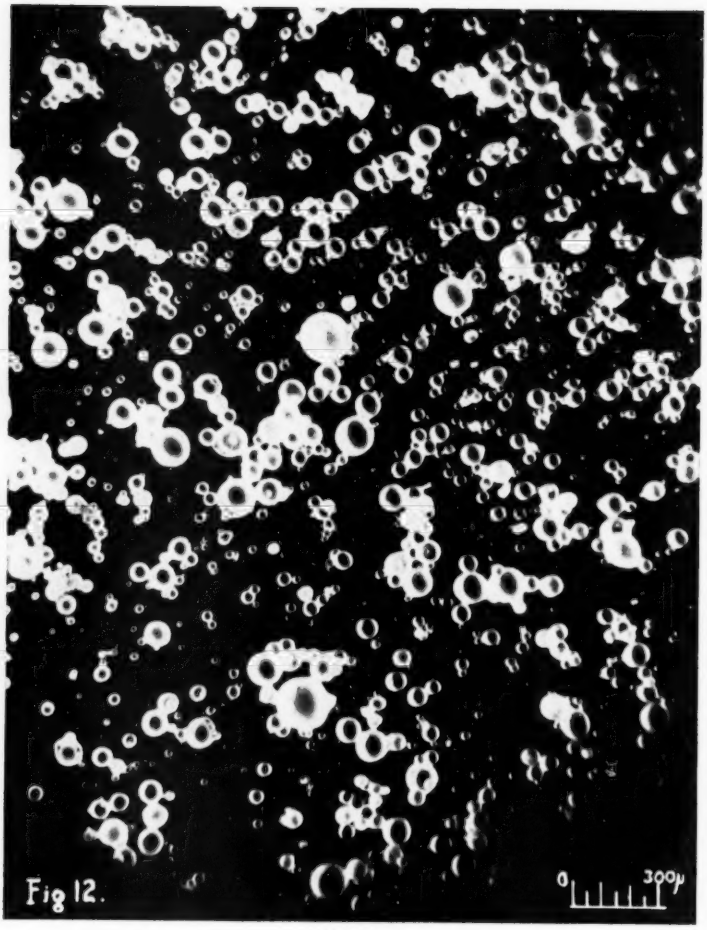

FIG 12

PHOTOMICROGRAPH OF WAX SPRAY DROPLET

Air Atomizers—Low Pressure Air

The range of firing rate with low pressure air atomizers is of the same order as that with the smaller medium and high pressure types, being about 5 to 1. As the atomizing air at low pressure is derived from a centrifugal fan, installation costs are relatively low and quietness of operation is a feature.

Ease of control is a notable characteristic, and this type of burner finds a wide application in industry in firing small and medium sized units, such as metallurgical furnaces and the like.

For rates of firing above about 500 lb fuel per hour, the centrifugal fan and the associated air ducting tend to become awkwardly large in size.

Pressure Jet Atomizers

This type is used almost universally under marine boilers, and in many large oil-fired land generating stations. A feature is its relative simplicity, no compressors or fans being needed for atomization.

For the controlled admission of the air for combustion a properly designed " front " or air register is required, similar to those used with high and medium pressure air and steam atomizers. This may operate with the natural chimney draught, or may be aided by induced or mechanical draught, depending upon the size and nature of the installation.

A satisfactory pumping unit is required to deliver the fuel to the burner, and in the case of the heavier grades it is necessary to pre-heat the fuel to reduce its viscosity to facilitate efficient atomization.

The scope of application of atomizers of this type is enormous, and they can be made in sizes handling a fraction of a gallon per hour up to single units handling 5 tons/hour.

A limitation, when using such atomizers singly, is the very narrow range of control, since the fuel output varies as the square root of the fuel pressure. Thus, if the minimum practical fuel pressure for atomization purposes is say 60 p.s.i., it would be necessary to raise the operating pressure to 240 p.s.i. in order merely to double the fuel rate.

In practice this limitation is sometimes met by applying a group of such burners to an installation, and controlling the rate of firing by cutting out or bringing in units as required.

Another way in which this limitation has been met is by the use of specially designed wide-range types such as the Peabody or spill burner, the Pillard or expanding slot burner, and the two-stage or duplex burner. A more detailed description of these types has been published.[1]

The Cost of Atomization

It is a simple matter to estimate the approximate net cost of atomizing a given quantity of fuel. For example, take the case of a pressure jet burner handling say 100 gal of fuel per hour, the fuel having to be heated from say 50° to 200° F to enable atomization to proceed efficiently. Assuming a pump pressure of 150 p.s.i. and a 50 per cent margin of excess pump capacity, 150 gal/hour would be pumped to a head of say 380 ft, requiring approximately 0·5 h.p. Only the fuel actually atomized would be heated,

i.e., 100 gal per hour raised 150° F representing a heat input of approximately 67,500 B.Th.U/hour, equivalent to approximately 19·5 kW. In all, it might be said that 20 kWh is required for atomizing this quantity of oil by pressure jet, equivalent to 2240 × 20 + 900 kWh/ton of oil. At 1*d* per unit, this represents a net cost of approx 4*s* 2*d* per ton. On the other hand, if the fuel were of a non-viscous grade which did not need heating, the cost would come down to a small fraction of this amount.

Other cases can be assessed on broadly similar lines and the approximate cost of atomization per ton of fuel estimated.

Such results may, however, be misleading, principally because of the wide variations encountered in the field in making a specific installation.

An alternative basis of approach is to assume that the installation is self-supporting, *i.e.*, that the power needed for atomization is drawn from the useful work performed in burning the fuel. For example, in the typical case of an oil-fired steam boiler, it may be taken that the boiler will generate 15 lb steam " from and at 212° F " for each pound of fuel consumed. On the basis of the cost per ton of the fuel, and the proportion of the steam generated which is ploughed back to provide both for pumping and heating it, a figure for the cost of atomization can be obtained. In the particular case stated, the cost of heating and pumping would work out at approximately 1*s* 6*d* per ton of fuel. An assessment on such lines of the comparative cost of atomization by the various systems already described indicates that there is very little difference in cost as between the pressure jet and the low pressure air types.

The medium pressure air or steam systems involve a cost about 30 per cent higher than the pressure jet.

The high pressure steam and air types come next, the latter involving the highest cost for atomization, which may be as much as three or four times that of the pressure jet or L.P.A. types.

Choice of Atomizer Type

The cost of atomization is generally a very secondary factor when it comes to the matter of choosing which type of atomizer to employ in an installation.

The various types have been developed not to compete with one another, but to meet the varying needs of industry, and to take advantage of available facilities.

In a works where steam is already available it would be logical to take advantage of this fact when installing liquid fuel fired equipment by adopting steam atomizers of either medium or high pressure type, according to the circumstances. Where a compressed air service exists, medium or high pressure air burners would naturally be considered.

If neither steam nor air services exist at the site, consideration would then be given to the use of small motor driven units, which would leave open to choice the pressure jet, the L.P.A., or the rotary burner.

However, in some circumstances the final decision as to which type to adopt may be primarily governed by technical considerations, based on experience as to which system is best suited to the given process or application.

Features of Good Atomizers

The quality of an atomizer cannot be judged by its external appearance or finish. Ultimately the only proofs of its merit are to be found either in an appraisal of its behaviour in operational service, or else as a result of quite searching laboratory tests, to which some reference will be made later.

However, it is possible to draw up a list or specification of the main features which one would expect to find in a dependable atomizer :

(1) It must atomize the fuel efficiently over the required operating range;
(2) The atomized spray should be discharged from it in a uniform or symmetrical pattern, suited to the application in mind;
(3) If of " two-fluid " type, it should not require an excessive quantity of the agent (air or steam) to effect proper atomization;
(4) It must perform reliably and constantly, and not be of itself susceptible to fluctuations or stoppages;
(5) It should preferably be of simple design, consistent with meeting performance requirements;
(6) It should be robust, without being clumsily heavy;
(7) It should have a long service life.

The extent to which an atomizer or burner meets the first six of these requirements is soon determined in practice on the installation to which the burner is applied. As regards the last item time alone will show with what frequency spare parts may be needed, and what steps can be taken to prolong their life. The performance of an atomizer must be judged critically. A visual inspection of the spray produced may serve to indicate how balanced or uniform this is, or else may reveal at once the existence of non-uniformity, streakiness, or even parasitic drip. However, it is as well to bear in mind that the most perfect atomizer cannot by itself give efficient combustion. It is essential to provide a properly controlled air supply to the spray. Having established, therefore, that the atomizer performs efficiently, it may then be necessary to look elsewhere for the explanation of poor or inefficient performance, which may arise from unbalanced or ill-guided air supply, or from other causes not attributable to the atomizer itself.

The Testing of Atomizers

The extent to which atomizers are subjected to systematic testing depends very largely upon their particular application. For example, a simple pressure jet or two-fluid type atomizer for general commercial and industrial use may require no systematic performance tests when once its fundamental design has been established and its production properly organized. All that may be necessary after assembly is a check on the soundness of any joints or glands which may feature in its construction. On the other hand, for certain applications atomizers may have to undergo rigorous inspectional scrutiny, flow testing to determine output characteristics, special tests to determine spray pattern uniformity or symmetry, and perhaps also examination in respect of the actual quality and mean fineness of the fuel spray they produce at one or more levels of output. In the routine proving of ordinary duty atomizers, testing requirements can usually be met by the provision of means of supplying the atomizers with

fuel under pressure, or fuel and agent if it is of two-fluid type, and a safe place where the spray can be projected and critically examined by eye.

For output measurements, various simple means can be used, such as the collection and weighing of the fuel discharged in a given time, or fuel measurement by meter, or by dip-stick in a small supply tank. For two-fluid types it may be desirable also to measure the mass flow of the atomizing agent, again by quite well-known means.

Spray Pattern

For the more elaborate tests, such as spray-uniformity and droplet-size measurements, highly specialized equipment is necessary.

The atomizers used in jet and turbine propellor engines are commonly subjected to spray-uniformity measurements in an apparatus to which the name " Patternator " has been given.[2] In this apparatus the atomizer is located above a sectorially divided circular collecting tray with partitions several inches high defining the sectors (usually twelve in number) into which it is divided. Each sectorial compartment is drained into a separate collecting vessel or burette. On test, the atomizer is fixed above the tray exactly coaxially at a height of from 6 to 12 inches, and the spray from it is thus collected in the twelve geometrically identical compartments, each of which yields to its burette the share it collects. The atomizer performance is then assessed on the basis of the relative uniformity in quantity collected from each sector.

Such a test is very necessary in the case of atomizers for aircraft engines, because unbalanced spray distribution may cause serious trouble in the very restricted combustion space invariably associated with such engines. It may be added, however, that an evenly distributed fuel supply from the atomizer is not by itself enough : it is also necessary in these high combustion–intensity applications to ensure also, what is usually more difficult, a balanced distribution of the combustion air to the fuel spray, and only by close attention to both aspects of the matter can efficient combustion and reliable operation be achieved.

It is the author's view that an extension of the Patternator test to commercial and industrial atomizers, with an appropriately modified scale of tolerance, merits serious consideration. The principle of the apparatus is obviously quite readily adaptable to suit the various types and sizes of atomizer which are commonly used.

In these days of high fuel prices and in some cases of restricted supplies, the tolerance of any avoidable waste in their use is to be regarded not merely as foolish, but rather as a folly verging on criminal.

It does not require the services of a fuel economy expert to reveal that an atomizer which sprays badly, or even one of which the spray is good only in parts, must inevitably be inefficient, either because it leads to incomplete combustion of the fuel or because to obtain complete combustion with it requires the use of an extravagant excess quantity of combustion air, with the heavy losses this entails. There is no doubt that a general check-up by users of atomizers in respect of their spraying performance, particularly in respect of spray evenness and freedom from heavy streaks (as judged by a simple visual inspection of the spray produced), coupled in some instances

with a patternation test and a check-up on combustion air supply in respect of reducing wasteful excess, would lead, on a very sober estimate, to a saving of many thousands of pounds sterling each year in the U.K. alone. If fuel consumers had also to pay for their air supplies, it would certainly have a magical effect in reducing fuel wastage.

Spray-particle-size Measurement

The detailed examination of fuel sprays, composed as they are of a wide range of sizes of very small droplets, is a highly specialized matter, and one which has been approached in many different ways. There exists quite an extensive literature to which reference can be made by any concerned with the subject.

Brief mention may be made of some of the better known techniques.

Possibly the most widely used method is that of projecting the spray over a target area consisting of slides coated with a uniform layer of soot or magnesium oxide. The spray, falling on the slides, penetrates the coating, leaving many crater holes, each in some degree commensurate in size with the particular droplet that made it. A microscopic examination of slide areas, coupled with crater measurements and a size-group tabulation, gives data upon which a statistical estimate of mean drop diameter or other features of the droplet-size distribution can be determined.

Another approach has been made by collecting the spray droplets in a non-miscible matrix liquid in which they are enveloped, but retain their spherical form and remain discrete. Microscopic measurement and counting ensue. This technique has been widely used with water sprays. Spray photography has been exploited by some investigators, with varying degrees of success.

A method at present favoured involves the use of a substitute material for the fuel or other liquid normally handled by the atomizer in service.[3]

In the case of liquid fuel atomizers, paraffin wax is used. If this substance is melted and superheated, the viscosity of the liquid fuel can be exactly simulated by it, and there is relatively little difference in the surface tension values.

By feeding the atomizer on test with liquid paraffin wax a quite normal spray is produced, and the liquid wax droplets freeze solid in flight very soon after their formation. A sample can be collected on slides, examined, measured, and counted.

Alternatively, a much larger bulk sample can be collected in water and sorted into size-group by passing it through a succession of graded gauze-sieves. The spray-size characteristics can then be derived from the weight size-group data.

In this way the comparative atomizing qualities of different atomizers under like conditions may be examined, or the effect of changes in operating conditions, such as rate of flow, atomizing pressure, or viscosity of the fuel, on any one atomizer may be determined.

Not all atomizers are subjected to particle-size-measurement tests. Usually one only of a new type is examined in this respect, so that the effects of design modifications or new features can be gauged.

A typical wax-droplet spray photograph is shown in Fig 12.

Factors Affecting the Quality of Atomization

(1) *Burner Design Factors*

In general, the two-fluid types of atomizer tend to give more finely atomized sprays than the single-fluid or pressure jet atomizer. The difference between the two types in this respect is relatively narrower in the small output sizes, and tends to become somewhat greater as the scale of capacity increases.

The quality of atomization with all types depends greatly upon details of design and highly accurate finish in manufacture. Symmetry of fluid flow is of great importance, and in the case of the two-fluid types this calls for accurate alignment or co-axiality of the steam or air channels with the fuel ducts or passages, so that a balanced and uniform confluence of the two fluids is achieved.

Again, with the two-fluid types, the quantity of the agent fluid per unit quantity of fuel materially affects the spray quality. Reducing the quantity of agent too far will result in incomplete entrainment and break-up of the fuel, and may give rise to heavy drooling or dripping.

Increasing the relative quantity of the agent generally improves atomization, but for practical purposes and for economic reasons it is rarely necessary to exceed the order of relative proportions given earlier.

Evidently one criterion by which two-fluid atomizers could be compared would be in terms of the agent to fuel mass flow ratio for equal performance.

The scale of physical size of burner in the case of two-fluid types does not appear to have a very marked effect on the fineness of spray, but in the larger sizes it may be found that a somewhat greater relative proportion of atomizing agent per unit quantity of fuel is required for optimum performance.

With the single-fluid or pressure jet atomizer, according to duty or output required, physical size is of material importance in respect of the fineness of atomization. A review of available test data indicates that the mean droplet size in the sprays produced varies approximately as $\sqrt{d}$, where d is the diameter of the discharge orifice. On the other hand, the actual operating pressure is of corresponding importance, the mean droplet size varying approximately as $1/P^{0\cdot4}$.

(2) *Fuel Factors*

With one very important exception, the effects of fuel characteristics on the quality of atomization are very small. This exception is viscosity. Whatever the type of burner, it is obvious that the fuel must at least be fluid enough to flow freely into and through it to the point where the atomization process occurs. A substance like a paste or a grease could be pushed through most burners, but it must be fairly evident that atomization would be difficult if not impossible with materials so highly resistant to flow.

A somewhat easier (more fluid) substance, like syrup, may be considered, but here again its viscosity, or resistance to flow, will be too great for effective atomization by normal economic means.

Rather than work on it with vast force in the form of immense quantities of very high pressure air or steam, or extremely high hydraulic pressure,

the simple alternative is to reduce its viscosity by pre-heating until it will flow quite freely. The fuel can then be handled by normal atomization processes in normal types of atomizer with the normal expenditure of force.

The actual extent to which viscous fuel oils must be pre-heated to enable them to be atomized varies considerably, and depends in the main upon the fuel itself, and upon the capacity, output, and type of the burner.

With the smaller pressure jets, the fuel viscosity in the burner should preferably not exceed 50 to 70 sec Redwood I (say a maximum of 15 cs), rising to a limit of 100 sec (23 cs) for larger sizes.

With two fluid atomizers a little more liberty may be taken, but in general it is more economical to increase the pre-heat of the fuel than to use more atomizing agent, and it is suggested that the viscosity level limits given above may with advantage be regarded as applicable to these types also.

Conclusion

Efficient liquid fuel burning by the process of fuel atomization has quite a long history behind it, covering nearly a century from its first exploitation in Europe and its later spread to the United States of America.

In this time, various designers have applied themselves to the many problems inherent in the art, and the present author could readily have multiplied the number of his illustrations five- or six-fold to exemplify the many detailed and sometimes quite subtle artifices which they have tried in developing atomizers of the various types without exhausting the subject.

However, in this paper only a very broad survey has been attempted, and any concerned to pursue the matter in more detail must be referred to the available literature.[4]

Digressions into the field of combustion and its problems have been avoided as far as possible, but it must always be borne in mind that the only reason for atomizing liquid fuels is to prepare them for combustion, which can be efficient only if the atomization is properly effected, and when proper skill and care are used in mixing with the atomized spray a regulated supply of air.

Acknowledgment

The author wishes to express his thanks to The Shell Petroleum Co. Ltd. for permission to publish this paper.

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Discussion

Mr Joyce, amplified the written paper considerably in his presentation of it and then exhibited a film entitled "Atomization," which told the story in simple language. The commentator pointed out that one of the main reasons for atomization is to spread a liquid, which was illustrated

by pictures of the spraying of crops and trees, with equipment carried by the user or mounted on a motor car or tractor.

Illustrating the function of the air in the burning of liquid fuel, the film showed that when a lighted taper was dipped into kerosine it was extinguished immediately, whereas when the kerozine was atomized it would burn. A drop of oil having a surface area equal to that of a postage stamp had, when atomized, a surface area equal to that of a double page of daily newspaper.

Types of atomizers were demonstrated, and details of their functioning were shown by means of equipment made of transparent material. A slow-motion picture was included to show what happened when a liquid was rotated at high speed in a cup. First the liquid was spread out in a film, then the film became so thin that threads of the liquid broke off the edge, and finally the threads broke into drops. But there was still the difficulty that the threads were flung far and wide, and the necessity for accurate design and workmanship was emphasized, for otherwise the direction and shape of the spray was affected. It was also emphasized that if the pressure of air applied to an atomizer were too low, the drops became too large and, if the sprayed oil were used as fuel, the flame would go out.

R. P. FRASER : Mr Joyce has put together a most useful survey of the factors which should influence us, not only in choosing the right burner for the right job, but in effecting improvements in the efficiency of operation. During his discourse he has filled in many of the gaps to which I was intending to point in the paper. He had filled in the gaps in connexion with variable flow pressure jets which have been so adequately illustrated in the film as being very important in aircraft. But I will point to one or two matters which may still have been missed; appreciating, of course, that no paper of this character, dealing with such a wide subject, can cover all its aspects.

I am perhaps a little confused about the paper. Does it deal with atomization at large, or with atomizers for liquid fuel, because quite clearly atomization is entering more and more into industrial processes to-day? Nevertheless, much of the content of the paper, although given to us under the heading of " Methods of Atomizing Liquid Fuel," can be referred, of course, to the atomization of other liquids.

Without wishing to be regarded as too much of a purist, I always find it difficult to accept the word " atomizer " as synonymous with " burner." A burner has to be an atomizer, but an atomizer is not necessarily a burner. In oil-burning technology it has become common practice, unfortunately, to use the two words as having the same meaning. I personally prefer to call the burner the entire assembly on the front plate of the boiler, including the secondary air director, and to refer to the fuel disintegrater only as the atomizer. Nevertheless, the author has given a fairly clear definition in his description of " atomizers for oil firing."

Several attempts have been made to classify atomizers into groups or categories in order to make them reasonably intelligible. The " two-fluid atomizers " referred to in the paper are also very often called " blast atomizers." Then we have " mechanical atomizers " and " pressure atomizers," and perhaps those three groups represent the best way of

dealing with them, although the last two may have air blast associated with them.

There are, possibly, three more kinds of atomizer—one of them falling into each group—to which the author has not referred.

First, under the heading " two-fluid atomizers " he has not mentioned a type of medium pressure air atomizer which has become known as the vortex cup type, and with which I have been concerned quite considerably. This is neither a true external mixer nor an internal mixer. It is a quite characteristic type because it employs the principle of a vortex ring in the air or gas stream on the nose of the nozzle, rather than the cylindrical vortex which is common in most atomizing devices. The vortex ring causes the central core of oil issuing from the orifice to spread out over the surface of a cup constituting the face of the nozzle, and on leaving the edge it meets the annular air stream. Thus the liquid is filmed before it is disrupted by the airstream. Because the contact time of the air and oil stream is prolonged, atomization is improved.

In the normal air atomizer, on the other hand, there is a solid rod of oil in the middle of the normal expanding air jet, and this is pinched off in a series of sausage-like pieces which later break up.

Plate 1(A) shows the old-fashioned type of medium pressure air atomizer where the air annulus is close to the liquid jet. The liquid jet is broken up first into chunks and then into relatively large drops and the distribution of fuel in the cross-section of the cone of spray is heavy in the centre and light at the sides. By means of the vortex cup nozzle form, Plate 1(B), finer atomization can be achieved using the same quantity of air, and better cross-sectional distribution than with the old-fashioned type. The metal around the jet is hollowed out so as to have an annular saucer around the orifice. Air issues from a narrow annulus around the edge of the saucer and, due to the high velocity air coming from the annulus, a vortex ring motion is caused to occur in the saucer. The vortex ring cannot move forward away from the nozzle and be lost, because it cannot penetrate the high pressure zone caused by the converging airstream from the annulus.

Fig 1 shows the pressure contours in p.s.i. in the cross-section of the airstream on the nose of such an atomizer. The low-pressure zone of the vortex ring is clearly seen. When used as a burner the metal of the jet forming the saucer round the orifice is kept quite cool by the oil passing through the centre and the air passing round it.

The second type falls into the second group, that of " mechanical atomizers," and here I refer to the spinning disk type rather than the spinning cup. The flat disk instead of the cup gives the advantage that a fairly uniform spectrum of drop sizes can be obtained under controlled conditions. Perhaps it is not quite fair to include this, because nobody has yet used the spinning disk effectively for atomizing oil in a fuel burner; but I think it could be designed for use in small combustion burners.

When the quantity of liquid is small the film on the disk is thin and the drops form at the edge of the disk, breaking away to form a major and minor drop only. As the quantity of liquid on the disk is increased, threads form at the edge of the disk, and these break down into a wider spectrum of drops.

When the disk is loaded with a much greater quantity of liquid there is

an interesting phenomenon. The liquid film edge has lost the support of the disk, and there is a freely expanding film of liquid outside the disk. Holes can appear in the film, and under the influence of surface tension there is contraction of the edge of the hole, so that the hole enlarges and disrupts the disk of liquid; whereupon the free edge becomes very ragged, is no longer circular, and a still wider spectrum of drops is formed. If the speed of the disk is increased, then air resistance plays a large part in the disintegration of the film.

In a commercial form of atomizer for spray drying, the disk is hollow, and it has window ports on the periphery. Each window has a film of

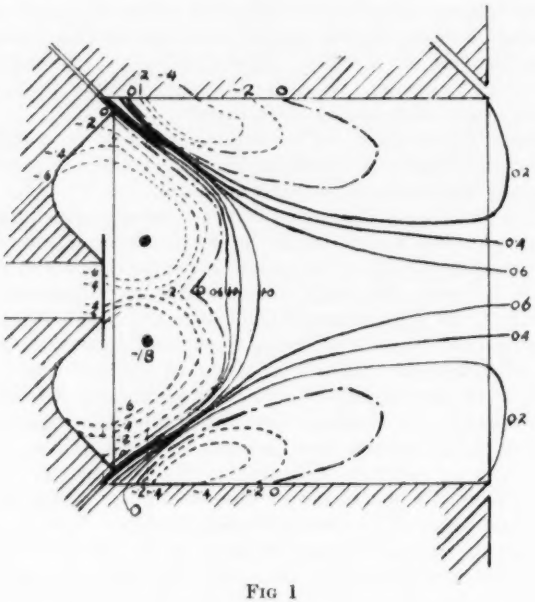


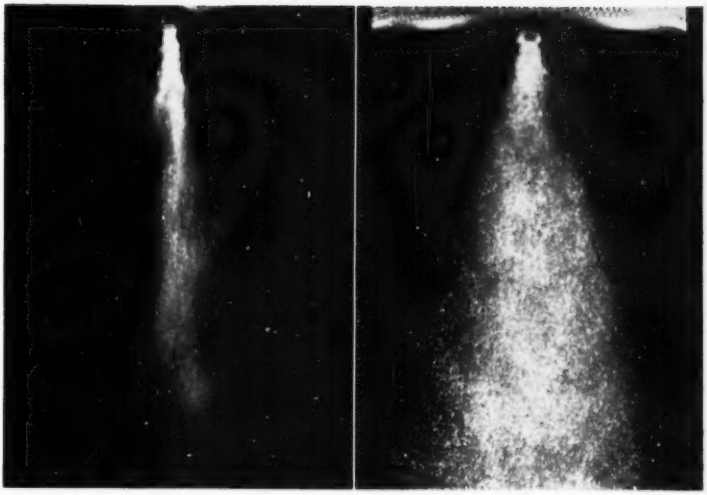
FIG 1

liquid around its edge and, thus, the equivalent of a very large disk is produced.

The third type falls into the author's third group, that of "pressure atomizers." I refer to the simplest of all types of atomizer, the single hole orifice, designed to give a fan-shaped sheet spray. This type is now used very considerably for small volume spraying of insecticides and other liquids.

It has not yet been used very much, to my knowledge, in oil flame devices; the nearest approach is the single hole orifice used in injection gear for engines. I really mean the single hole orifice where the liquid is made to film outside the orifice, by shaping the back of the orifice in a manner to produce a fan-shaped spray. These fan-shaped spray nozzles are extremely cheap to produce.

It always seems to me that this provides a possible line of attack in flame



A B

A. Sharp-edged air orifice with solid liquid jet at centre
B. Vortex cup type nozzle

PLATE I

MEDIUM PRESSURE AIR ATOMIZERS OPERATING WITH AIR AT 5 P.S.I. AND WATER 5 G.P.H.

[*To face p.* 74.

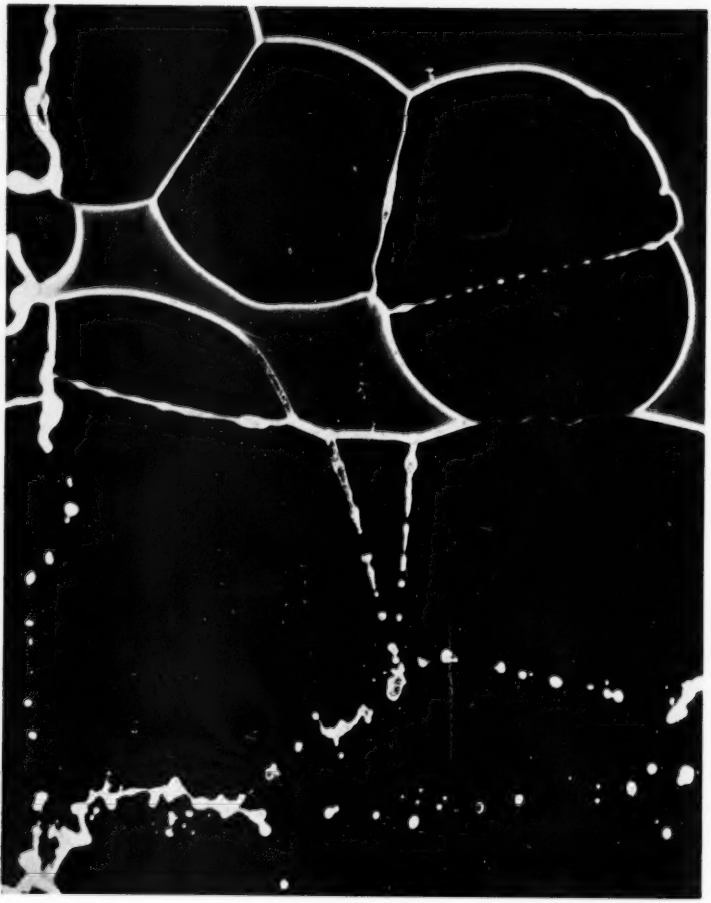


PLATE II

devices for burning fuel oil. I am particularly interested in this type of atomizer, because it enables us to examine the manner of disintegration of a sheet of liquid much more easily than other types because the sheet is in one plane.

Plate 2 shows the effect of increasing pressure on the manner of disintegration of the sheet. At low velocities with pure liquids a placid film is produced and eventually radial waves form in the sheet and the sheet disrupts uniformly at the leading edge. With higher liquid velocities, air resistance and air disturbances play a greater and greater part until, at very high velocities, it is mainly responsible for disintegration.

With impure liquids holes may appear in the sheet at quite an early stage and these expand until threads of liquid are formed between them; these threads become stretched and eventually break down into drops. The photograph shows the disintegration of the threads into drops by this stretching process.

Where drops are formed from threads themselves, they are fairly uniform and in two sizes, a major and a satellite drop. Where the drops are formed from the junctions of threads they are much more varied in size and, generally, a good deal larger. This instantaneous photograph shows the varied stages of breakdown of the threads and illustrates one large island of liquid which will later break down into larger drops.

With regard to the cost of atomization, the important thing to remember, I think, is that all atomizers are pretty inefficient machines—and that is true also of almost all grinding apparatus. If this parallel with the grinding machine is correct—and I am inclined to think it is—then the amount of energy required is roughly proportional to the amount of new surface created. Inasmuch as the surface–volume ratio of a particle increases extremely rapidly as the particle becomes smaller, clearly there is an economic limit to the atomization of the liquid. I have grave doubts that in a fuel device it is necessary to reduce the particles to extremely small sizes, because the rate of evaporation is very much increased and if sub-micron particles are produced the fuel will be operating in the gaseous state, and I am sure that in many boilers that would not be of advantage. I think there must be a definite particle size in order to obtain the best combustion.

On the question of the application of the energy for atomization, the most economic energy that can be applied is that in the form of heat to reduce the viscosity of the fuel; so that I am in complete agreement with the concluding words of the author that "viscosity should be reduced to the lowest possible limit before it enters the atomizer."

MR JOYCE: In extenuation of my several omissions from the paper I would say that, had I tried to include every type of atomizer known to me, it would have been several times as long as it is. I know of the vortex ring type of atomizer, and believe it to be a very effective one. I was very interested to hear from Dr Fraser how it works. I gather that there is a sort of toroidal ring of gas flow around the atomizer. But the filming of the liquid across the shallow annular valley makes me wonder whether in practice such a burner would give rise, at least in certain applications, to very severe carbonization on the burner face. In gas turbine atomizers

there is need to provide a strategic feed of air across the face to inhibit carbon deposition, and I am led to wonder whether this deliberate wetting of the annular valley in the vortex ring type of atomizer might in certain circumstances lead to an early call for service.

There is really no fundamental difference between the spinning cup and the spinning disk, which is used widely for drying slurries for packaging.

In respect to Dr Fraser's comments about the possibility of the wider exploitation of the spinning disk as against the spinning cup, and his reference to the fact that with the spinning disk a uniform size of particle or a spray composed of a sensibly uniform size of particle can be obtained, I am a little in disagreement because all the information I have of spinning disk and spinning cup atomizers indicates that a uniform size of particles is obtainable only if they are starved of fluid. If that is done and an atomizer of that type seen at a fantastically high rate of rotation, particles can be obtained, broadly speaking, in one narrow spectrum of sizes. But otherwise there is a wide spectrum of sizes. It is my experience, that as the cup is fed at combustion rates of firing it begins to perform in the manner of other types of atomizer. So that the fact that, under special conditions, particles of one size can be got seems to be more or less of academic interest from the fuel-burning point of view.

I believe there may be special applications where a fan-shaped spray will have advantages; but generally speaking it is convenient to spray in a circular manner. I presume that with a flat spray one would have to take special care to provide perhaps two streams of air, in order to effect proper mixing.

With regard to viscous liquids, those concerned with fuel firing are sometimes told by various people that they have a burner which will handle pitch cold. But always eventually it is necessary to apply heat. The simple way out of such a difficulty is to preheat the material until it flows freely. Heated adequately it will yield to the gentle persuasion of air or hydraulic pressure.

G. J. Gollin : There is an interesting type of burner not referred to in Mr Joyce's paper. I have always called it an " injector," because if it is used to spray fuel into the combustion chamber of a shell type boiler, the fuel will not burn. A spray of oil is produced, but as soon as the lighting up torch is withdrawn, the flame disappears. However, these injectors are very important devices for firing furnaces; once the temperature of the furnace is raised to 500° or 600° C, the sprayed fuel from such an injector will give a steady flame.

Most people, myself included, used to think that the reason why these injectors would not maintain the flame in a cold environment was that the atomization was bad. Fortunately, however, the International Flame Radiation Committee wanted to know what was the size of the droplets from these injectors, and Mr Joyce was asked to examine a series of them. To my surprise, the atomization was found to be extraordinarily uniform and fine; I think it beats easily the average pressure jet of the same size in that respect. So that the reason why the spray from such a burner will not remain alight is not that the drops produced are too large.

The real reason may perhaps be found if it is considered why the fuel

from an ordinary burner, other than an injector, remains alight. I think the reason is mainly that the droplets are rather like onions, having outer layers and, when using an ordinary burner, the droplets, before reaching the flame, have time to have those outer layers peeled off and vaporized, and they can then catch fire. But when the droplets leave an injector at a speed of 400 ft/sec and it is tried to establish a flame front 5 ft away by means of a torch, there is not time for the outer layer to be peeled off and to ignite the droplets.

During the war it was discovered that it was possible to set fire to several pieces of wood only if the distance between them was not much more than the thickness of each piece. I have come to the view that a flame front can only be established in a mass of burning droplets provided the distance between the droplets is not more than a certain number of times their diameters. Again, in a burner arrangement which produces a stable flame there is usually a strong current backwards towards the nose of the burner; but if the droplets have to travel 5 ft in order to warm up until they will catch fire, you cannot have that backward current at that distance from the burner.

Nevertheless, these injectors are of very great importance for use in high temperature furnaces. Usually they use about 10 ft/lb of momentum per lb of oil; and an important point is the way in which they bring in the air for combustion. This type sucks the combustion air into the flame rather slowly by the initial momentum of the atomizing fluid. From Mr Joyce's remarks on the choice of burners, I think that first a burner should be chosen with as little atomizing medium as possible, and secondly one which will bring the air into the flame in the required manner. So that for temperature furnace work these injectors have an advantage.

In my opinion the mechanism of the vortex burner referred to by Mr Fraser is the same as in the spinning cup, except that in this case the cup is stationary and the oil and air are spun over it.

With regard to the pressure jet, it has been a source of irritation to me not to know why there is a wave form in the liquid film coming from the nozzle. The general opinion is that the air, rushing into the depression in the centre, plays a big part. I believe that internal pressure conditions fluctuate at a rapid rate and that the fluctuation is caused by some internal disturbance. Nearly all the magnified high-speed photographs of a spray show air bubbles in the film. If the size of the air bubbles is compared with the size of the swirl groove when the bubbles are going down it, it seems that the groove must be nearly empty. I would like to know whether anybody has tested a pressure jet burner where all the air has been very carefully removed from the fluid before it is passed through.

I believe it has been found mathematically by Dr Watson and others that a pressure jet burner atomizes best at an angle of something like 78° to 80°. That is all right in dealing with a water tube boiler, but in a combustion chamber of limited diameter, it may be necessary to mould the flame to suit the combustion tube by means of introducing the combustion air at a high velocity. In the ordinary shell type boiler, however, the air for combustion is brought in by natural draught or induced draught through the air registers at speeds which may be as low as 50 ft/sec. The alternative usually adopted by the burner makers is to modify the characteristics of the

atomizer so as to provide for such cases a narrow angled spray of, say, 50° or 60°. I think this gives coarser atomization and makes it more difficult for the air to get into the spray. They must, however, choose between having fine atomization and hitting the wall of the furnace or missing the wall and having coarse atomization.

I believe there is a good future for the hybrid (pressure jet and blast) burner where you have to complete the combustion of 1 or 2 tons of oil per hour in a distance of about 20 ft. The small amount of compressed air or steam reduces the particle size and makes it possible to finish the flame in a shorter time.

When assessing the cost of atomizing a heavy oil in an industrial organization I think it should be taken into account that a heavy oil cannot be pumped unless it is kept in a preheated storage tank, and if the oil is maintained at a temperature of about 100° F, even where tanks are well insulated, the cost of so doing adds a fraction of 1 per cent to the cost of handling.

MR JOYCE : I am very glad to have Mr Gollin's comments on the payer. I am aware, of course, of the existence of the injector type atomizers, and their extraordinary power of atomizing has been revealed to us recently by tests.

Reference has been made by Mr Gollin to the air bubbles seen in photographs of the film coming from a pressure jet burner. Although I am not able to offer specific proof, I have a theory that these air bubbles in the film do not derive from air flowing into the atomizer; in other words, that they have never seen the grooves. I believe they derive from the air core. In the pressure jet atomizer the highest rotational speed is at the air–fuel interface in the air core, and the lowest rotational speed at the wetted surface of the orifice. I am speaking now of the region of the orifice. The air core goes down and spins on the rear boundary wall of the vortex chamber; in examining a large model of a pressure jet I have seen a lot of turbulence where the air core terminates on the back boundary of the vortex chamber, and in so far as the flow there is of a boundary layer character, I believe it is quite possible that some air, in small bulk, may be whipped up from the disturbed base of the air core and entrained in the film which is subsequently produced.

Regarding the question of firing industrial apparatus, and the optimum spray cone angle, that is a theoretical consideration, which is borne out in practice only to a small extent. There may be optimum atomization at an angle of 85° to 90° when a pressure jet is operated at extremely low fuel pressure. When operated at normal working pressures round about (say) 100 p.s.i. and above, the difference in spray quality over the range from 60° to 100° ceases to be significant, but the spray angle itself may be.

Another point I would take up is the reference to 50 ft/sec as the limit available for the introduction of air for industrial oil firing. That strikes me as being extremely small; I believe that velocity indicates a pressure difference of something well under 1 inch water gauge. I think Mr Gollin might consider using velocities up to 150 ft/sec, in which case he will probably find that he is able to stabilize his flame rather closer to the burner than he considers possible at the moment.

I agree that the air pressure jet offers not only a chance of enhancing the quality and fineness of atomization by large scale pressure jet burners, but it also provides an attractive means of obtaining a wider range with pressure jet burners of any size.

The point Mr Gollin raised about the minute addition to the cost of atomization, due to the necessity of heating heavy fuel in storage, is accepted. The brief observations in the paper concerning the cost of atomization were put in merely to give an idea of the relative significance of things, and by and large the cost is not very significant. It represents a trivial increase of cost on the fuel; the choice of atomizer for a particular purpose is decided least on the basis of the cost of atomization, and more on the suitability of a particular type of atomizer for the purpose in mind.

DR J. S. CLARKE : I would like to draw attention to what I consider is an omission from the paper, namely some reference to the evaporation process of droplets, although I do realize that the paper is concerned in the making of droplets. I feel that it would have been helpful to any group of engineers if the order of the size and the time required for their evaporation had been included. For instance, in aero gas turbine practice the evaporation process must be completed in something of the order of 4 milliseconds. It is clear, therefore, that the spray does not exist for a very long period, probably not more than 2 cm, from the orifice. After that the mixing is generally due to the aerodynamic processes.

The example of the atomizer referred to by Mr Fraser appears to me to be wrong in principle from the point of view of that type of combustion. It seems to me (although I am not acquainted with the spray formation) that a fairly solid cone formation would emerge—I would submit that it would be rather difficult to mix properly the air and fuel without undue pressure loss. There also may be some difficulty with regard to the patternation. We used the flat spray atomizer in certain applications, and generally speaking found that its patternation is not so good as the swirl type.

MR JOYCE : Regarding actual combustion and rates of evaporation of fuel from droplets, I am afraid I shall have to ask for an alibi. The title of my paper is " Methods of Atomizing Liquid Fuel." Although I have mentioned several times the importance of a balanced air supply into the fuel, because it gives uniform and efficient combustion, I do not wish to be drawn into a controversy in the matter of the evaporation of droplets. At our Thornton Research Centre work on the subject continues, and a great deal of very excellent work on it has been done at the National Gas Turbine Establishment; I think most of the information gained is available. Therefore, I will not try to give data on evaporation, beyond making the more or less obvious statement that we never burn a liquid fuel as such, and the process of burning after atomization is the point at which I stop in this paper.

The process of burning is a vapour phenomenon; it occurs at the air–vapour or air–liquid interface. Vapour is formed around the droplet, and that is again surrounded by air, and at some region the mixture strength is within the limits of combustibility. One of the requirements is to suspend

the droplets in space, and we must allow for the continued supply of air for the completion of combustion before they strike any cold surfaces or metal surfaces.

E. M. GOODGER : With reference to the wax spray shown in the film there was an argument some years ago concerning the variation between the diameter distribution of wax and fuel droplets.

When plotted on the Rosin–Rammler axes, the wax droplet results appear as a straight line, but I think it will be found that the fuel droplet results, as obtained by the " impressions " technique, appear as an S-bend.

MR JOYCE : My first observation about the possible difference between a spray examined in the liquid phase and a spray of wax is that the sole reason paraffin wax was used for determining the spray quality or structure was that it offered the line of least resistance. At the time we were concerned mostly with a highly volatile liquid like kerosine, and found it very difficult to capture a representative sample of the liquid spray. The spray obtained with liquid wax had the same viscosity precisely, and almost the same surface tension, as the liquid fuel it purported to represent I cannot say that the spray we obtained was the same as a spray of liquid fuel. The most claimed for it is that it gives a useful means of comparing the performance of one nozzle with another or of one nozzle under a variety of conditions, and it will behave in the same relative way when using the legitimate fuel.

It is hoped to put the paraffin wax technique to the acid test of a very rigid comparison with a legitimate fuel, using the same atomizer under precisely the same conditions. The position at the moment is that we are using blends of wax whereby we can obtain viscosities which are outside the range of simple waxes. In other words, we want to make the waxes match the fuels, and then we can probably get a valid comparison.

A. H. TRAVIS : I am very pleased that Mr Joyce has mentioned the wax droplet technique for examining the size range of drops one may expect to find in a spray of fuel. This appears to be the most satisfactory way of examining a fuel spray; and has a very practical appeal to engineers in that they can collect all the spray from a single injection and examine samples to their hearts' content.

As mentioned in the paper, criticism is sometimes made that the viscosity of the fuel, which is reproduced by the temperature of the wax, is not the only factor influencing atomization, and that the important effects of surface tension are ignored. Mr Fraser has indicated the importance of surface tension effects. I would like to ask Mr Joyce if he sees any hope of meeting this criticism by testing with blends of wax which can be maintained at a constant value for viscosity and variations made in the values for surface tension. I appreciate that such blending will present many difficulties.

I have noted with interest the references in the paper to rotating burners. They appear to be so simple in conception that it would be interesting to have Mr Joyce's comments on why this system has not been more widely used; a series of concentric cups would appear to offer a possible means of providing a very uniform and wide distribution of fuel.

MR JOYCE : In regard to the control of surface tension, or at least the control of viscosity in order to determine surface tension effects, preparations are being made to work along those lines. Recently a series of wax blends were examined very critically. A range of blended waxes has been produced with which a range of surface tension of from 19 to 29 dynes/cm is obtained. There will be some modest change of density, but perhaps we can allow for that. At least we can hope to control the viscosity, which is the most vital physical characteristic, and to get some data on the effects of surface tension as an isolated factor.

Surface tension is not a matter about which fuel people need worry greatly. Most hydrocarbon fuels come within the range from 20 to 29 dynes/cm. Higher surface tension makes coarser, and lower surface tension makes finer, droplets, and it is our aim to assess its effect quantitatively.

On the question of the rotary burner in the gas turbine, a type of rotary burner was once tried in an experimental combustion chamber at Sir Frank Whittle's establishment during the war. It was an air-spun type of rotary atomizer; it had turbine vanes, and the moving air feeding into the combustion chamber spun the device, the fuel being projected through some orifices and caught up in the swirl. But a difficulty is that air-spun rotary burners cannot be depended upon for gas turbine combustion chambers. I do not think it is possible to ensure that air-spun cups will all run at the same speed and produce equal atomization. To have all the spinning cups running at the same speed requires mechanical drive to all of them. I think that is the simple answer to the question as to why they have not been used in aircraft gas turbine combustion chambers.

THE CHAIRMAN : I should like to thank all who have participated by contributing their remarks or asking questions; and on behalf of the whole audience and myself I express thanks to Mr Joyce for a very excellent paper, of high calibre.

(The vote of thanks was heartily accorded.)

A PRELIMINARY STUDY OF THE RHEOLOGICAL PROPERTIES OF RESIDUAL FUEL OILS IN RELATION TO THEIR COMPOSITION

By G. C. Ackroyd * and C. M. Cawley,* O.B.E. (Fellow)

Summary

The results are presented of a study which has been made of the anomalous behaviour of wax-containing oils. The fluidity of such oils is influenced by their thermal history, the sensitivity to treatment at different temperatures being greatly increased when asphaltenes and resins are present. A decrease in fluidity is associated with a decrease in the size of the wax crystals separating; for a condition of very low fluidity the crystals may be sub-microscopic in size. A wax-containing oil free from asphaltenes and resins may have considerable rigidity and a well-defined yield value. When asphaltenes and resins are present they may, under certain conditions, reduce the rigidity of the system by causing the wax to separate in the form of relatively large aggregates. Under other conditions the asphaltenes and resins may have little effect, as judged by pour point, or may substantially increase the rigidity of the system, as judged by yield value.

Introduction

The wax content of petroleum oils has for a long time been known to be an important factor in determining their rheological properties.[1-4] It is also generally agreed that the asphaltenes in residual oils play an important part, although the mechanism by which they act is uncertain.

Kolvoort *et al* [4] assume that asphaltenes or pour point depressants are adsorbed on the wax during the process of crystallization. It is their view that " in the presence of a suitable active body, the greater part of the wax nuclei will be coated with this active substance immediately on formation, and crystallization will take place on only a few nuclei which have escaped this action, or where ' weak spots ' occur. The result is in general the formation of a few relatively large crystal aggregates. Such a layer is repellant to oil, and is removed by the wax on filtration." In the absence of active bodies the formation is postulated of many nuclei, each of which grows into an individual crystal; if the wax is of the oil-retaining type, oil is adsorbed on the wax. When the crystals are in sufficiently close proximity, interlocking occurs.

Moerbeek and van Beest [3] consider that on cooling an oil containing wax and asphaltenes, the asphaltenes separate out on the surface of the wax crystals, thereby preventing the formation of a cohesive crystal structure throughout the oil. The influence of the asphaltenes on the crystallization of the wax is eliminated by a suitable pre-cooling, followed by preheating to such a temperature that the asphaltenes do not dissolve again.

Asphaltic bitumens are closely related in origin and composition to residual fuel oils; in general, the former contain a higher proportion of

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compounds of high molecular weight. Their content of asphaltenes is high, the range of 23 to 30 per cent being characteristic; the remainder consists largely of maltenes (*i.e.*, resins and less complex hydrocarbons or heterocyclic compounds). The mean molecular weight of the maltenes is 500 to 600. The range for the asphaltene content of residual oils is usually 2 to 8 per cent; the remainder consists of maltenes including 10 to 15 per cent of resins. The resin-free material may have an average molecular weight as high as 380. It is not unlikely therefore that many of the factors responsible for the rheological properties of asphaltic bitumen will contribute towards the properties of residual oils.

According to Pfeiffer [5] the asphaltenes are associated with high molecular weight aromatic constituents (resins) in micelles which constitute the disperse phase in asphaltic bitumen, the continuous, or intermicellar phase consisting of compounds of lower molecular weight. The micelles in the bitumen may either move freely with respect to each other or, by mutual attraction, they may form a structure throughout the bituminous mass. The colloidal state of the system thus largely determines the rheological properties of the bitumen. If the micelles are well peptized the bitumen behaves like a sol. If they are partly flocculated, a more or less rigid structure is apt to be formed, and the bitumen behaves like a gel.

The colloidal condition of the system depends upon the concentration and the chemical character of the two phases. According to Pfeiffer and Saal [6] complete peptization of the micelles is possible if the system contains enough aromatic constituents (resins), in relation to the concentration of asphaltenes, to saturate the adsorption forces of the asphaltenes. If, however, the aromatic content is not large enough to do this, mutual attraction between the micelles occurs and leads to the formation of a gel structure or the precipitation of asphaltenes.

The equilibrium between the asphaltenes and the peptizing bodies, being due to adsorption, takes time for completion,[5] and it is this which accounts for the effect of age on the rheological properties of asphalt. The position of the equilibrium and the time required to attain it also depend on the temperature, so that changes of temperature affect, among other things, the volume of the micelles.

On the subject of paraffin wax in asphaltic bitumen Pfeiffer [5] states that its influence is significant with respect to the rheological properties of asphaltic bitumens in so far as it is present in a crystallized condition at normal temperature. The crystallized wax may either form a skeleton structure which gives the bitumen a yield stress or be present as loose particles which only increase the viscosity as filler. Because of its wax content, the hardness of an asphalt rich in wax is very sensitive to supercooling.

Jones and Blachly [7] considered the difference between crystalline wax, easily separable from surrounding oil, and " amorphous " wax, from which the oil could be separated only with difficulty. They assumed that this is due to a surface tension effect, and in fact the general view has been expressed elsewhere [8] that the major portion of liquid in such systems is held by capillary forces. They further considered that the " degree of amorphousness " of the wax is related to the adsorption of some substance which is concentrated in the higher-boiling fractions of the oil. According

to Zimmer, Davis, and Frolich,[2] " Paraflow " is preferentially adsorbed by wax, reducing the size of the larger crystals and preventing the adsorption of large quantities of oil by the wax. Bondi [9] supports the idea of the preferential adsorption of Paraflow, and suggests that this can prevent the cohesion of the wax crystals to one another, and thus prevent the formation of a structure. The suggestion that the structure in a wax–oil system is due to lattice forces, the crystals actually growing into one another, has recently been put forward by Jones and Tyson [10] in connexion with their work with *n*-octacosane in a Pennsylvania neutral oil.

Williams,[11] working with concentrated suspensions of particles of various sizes and shapes, recognizes the present limitation of knowledge in this field, and states that a sound theory is still awaited to account for : (*a*) the forces between the particles of a suspension, tending to hold them together, and (*b*) the stability of a flocculate to the forces imposed upon it during shear.

An understanding of the rheological properties of wax-containing systems is of more than theoretical interest, since the behaviour of such systems creates problems in several fields of petroleum technology, particularly in connexion with the pumpability of waxy residual fuel oils. Because of the wide interest of this problem to users of Middle East oils, and especially its interest to the Admiralty, the work described in this paper was carried out in an effort to throw some light on the factors responsible for the rheological properties of these oils.

Description of Materials Examined

It was decided at the outset to study distillation residues, rather than blended residual fuel oils, in order that the asphaltene–wax–maltene system should be disturbed as little as possible. Three straight-run residues supplied by the courtesy of the Anglo-Iranian Oil Company Ltd., were accordingly used; they were obtained by the refinery distillation at atmospheric pressure of crude oils from three Middle East fields. The residues are referred to as Oils A, B, and C respectively. Inspection data provided by the Company are given in Table I together with pour point and other data determined at the Fuel Research Station. Table II summarizes the results of a more detailed examination of the properties of the asphaltenes from the three oils. The pour points recorded were determined either on the samples of oil " as received " that is, without the heat pretreatment given in the standard method (IP 15/42), or on samples subjected to a special conditioning treatment. This consisted in heating the sample to 160° to 180° F followed by shock cooling to −30° F. Immediately after shock cooling, the sample was preheated to a temperature between 70° and 140° F, and the pour point was determined when required by cooling in the normal way (IP 15/42). Unless otherwise stated, this treatment was used throughout the work to condition all oils before pour points or viscometric data were obtained.

The pour point data recorded in Table I are shown graphically in Fig 1 ; pour points obtained without any pretreatment except preheating to the temperature indicated are given in Fig 2. Both figures show that of the three oils, Oil A is the most sensitive to pretreatment, especially when this

TABLE I

Properties of the Residues Examined

	Oil A	Oil B	Oil C
Inspection Data :			
Volume on crude, %	50	49·6	52
Weight on crude, %	55·5	55·3	57·4
T.B.P. (cut point), ° C	285	340	286
Sp. gr. 60/60° F	0·931	0·935	0·935
Kinematic viscosity at 100° F, cs	93	710	158
Ultimate Analysis, % :			
Ash	0·02	0·02	0·05
Carbon	84·85	84·55	85·00
Hydrogen	11·85	11·35	11·90
Nitrogen	0·2	0·3	0·3
Sulphur (total)	3·1	3·8	2·2
Difference	0	0	0·6
Moisture	Trace	Trace	0·05
Molecular weight *	397	539	439
Pour point (as received), ° F	55	50	60
Pour point, ° F, after heat pretreatment at :			
80° F	40	50	—
90° F	55	50	75
100° F	65	50	75
110° F	65	50	—
120° F	40	50	75
130° F	0	45	—
140° F	−5	45	75
Asphaltenes (by IP 6/49), %	2·8	2·1	1·0
Wax (insoluble in CH_2Cl_2 at −25° F), %	10·3	9·5	12·6

* By elevation of the boiling point of benzene.

TABLE II

Properties of Asphaltenes

	Asphaltenes from		
	Oil A	Oil B	Oil C
Asphaltenes by precipitation with pet. spirit (IP 6/49), %	2·8	2·1	1·0
Description of asphaltenes	Black, brittle material	Black, brittle material	Brown, waxy material
Asphaltenes by precipitation with pentane (7½ : 1), %	5·8	5·9	4·1
Extraction of the 7½ : 1 Pentane Asphaltenes with Solvents :			
Soluble in 60° to 80° C light petroleum, %	18·9	17·6	27·9
Soluble in 100° to 120° C light petroleum, %	9·3	23·3	16·3
Soluble in dioxane, %	4·9	3·5	6·9
,, ,, ethyl acetate, %	6·7	7·1	5·6
,, ,, methyl ethyl ketone, %	47·7	14·9	1·4
Insoluble	12·5	33·6	41·9
Total	100	100	100

includes shock chilling. In contrast, Oil B is the oil least influenced by the temperature of pretreatment. Oil A was therefore selected for more detailed investigation, though some study was also made of Oil B.

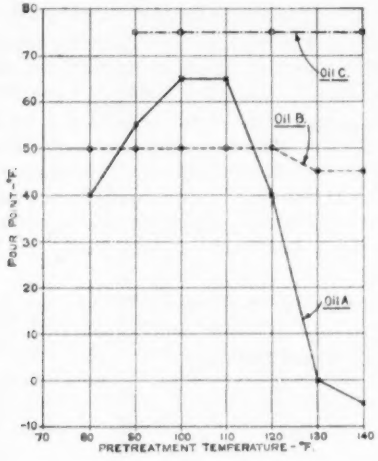

FIG 1

POUR POINT *V* HEAT PRETREATMENT TEMPERATURE FOR OILS A, B, AND C (AFTER SHOCK CHILLING)

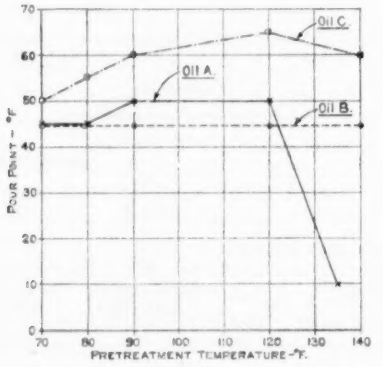

FIG 2

POUR POINT *V* HEAT TREATMENT FOR OILS A, B, AND C

In Table II are given the asphaltene contents of the three oils as determined by the standard procedure (IP 6/49) and by precipitation with pentane in the proportion of 7·5 parts of pentane to one part of oil—a procedure used in the present work for the separation of asphaltenes from the residual oil in bulk. The IP procedure includes the continuous extraction of the asphaltenes initially thrown down by the addition of petroleum spirit, with a further quantity of petroleum spirit, but this extraction was

not carried out in the determination of asphaltenes by means of pentane, and this latter method consequently gave higher values. The results of a subsequent extraction in a Soxhlet of the pentane-separated asphaltenes with various solvents are given separately in Table II. The results serve to show the complexity of the asphaltenes and the differences in the amounts of non-asphaltic material that may be associated with them; but the greatest differences disclosed by this extraction appear in the amounts finally obtained of the insoluble residues, which presumably represent the complex nucleus of the asphaltene micelle.

Separation of Oils A and B into Fractions

Having chosen the oils to be examined, the method described in the next paragraphs for the separation of their major constituents was devised to avoid, as far as possible, any treatment likely to produce permanent changes in the oils.

The asphaltenes were separated by the addition of $7\frac{1}{2}$ parts of pentane to 1 part of the oil; the mixture was refluxed for 3 hours, allowed to stand overnight, and the supernatant liquid was then decanted from the asphaltenes, which were washed with cold pentane until the washings remained colourless. The pentane washings were added to the decanted pentane solution, and the whole was refluxed for 3 hours, allowed to stand overnight, and decanted as before. The whole process was repeated a third time and the decanted pentane solution centrifuged to remove the last traces of asphaltenes. The asphaltenes were collected together in solution in benzene, an aliquot of which was used in order to estimate the percentage of asphaltenes obtained by this procedure. The oil freed from asphaltenes, hereafter called deasphalted oil (pentane), was recovered from its pentane solution.

It was expected that this separation with pentane would remove the higher molecular weight constituents, but for the complete removal of resins it was necessary to carry out an extraction of the deasphalted oil (pentane). For this purpose three parts of activated alumina to one part of deasphalted oil (pentane) were taken; the oil was dissolved in benzene and the alumina added to this solution with constant stirring. The benzene was evaporated off on a water-bath (final traces being removed in a vacuum oven), leaving the oil adsorbed on the alumina. This material was then extracted with pentane, giving a yield of extract of over 85 per cent for Oil A and 81 per cent for Oil B, calculated on the original oil. It was considered that this extract (hereafter called " pentane extract from alumina ") was entirely free from asphaltenes and resins. The alumina was further extracted with benzene followed by an azeotropic mixture of benzene and ethyl alcohol; this gave two small fractions of a black pitchy material, and there was a considerable proportion of the oil which could not be extracted by solvents from the alumina (7·7 per cent calculated on the original oil in the case of Oil A).

The pentane extract from alumina was shaken with five times its volume of acetone and allowed to stand for two days. The material soluble in acetone was decanted off and the acetone-insoluble material washed with fresh acetone. The acetone was removed from both fractions by evapora-

tion to constant weight on a water-bath. This treatment resulted in a concentration of the wax hydrocarbons in the acetone-insoluble fraction.

Both fractions were treated for the removal of straight-chain hydrocarbons through the formation of the urea complex.[12, 13] *iso*-Octane was found to be a satisfactory solvent for the dilution of the oil, and also for the subsequent washing of the complex.

After removal of the straight-chain hydrocarbons from the acetone-insoluble fraction, further dewaxing of this fraction was carried out, first with methyl ethyl ketone and, secondly, with a 4 : 1 mixture of acetone and methylene chloride.

Tables III and IV give detailed weight balances of the separations carried out on Oils A and B, together with analytical data on each fraction; the variation of pour point with the temperature of pretreatment of the fractions is shown graphically in Figs 3 and 4. The amounts of asphaltenes separated by pentane treatment from Oils A and B and reported in Tables III and IV respectively are lower than those reported in Table II. The actual figures are 4·5 per cent and 5·8 per cent for Oil A and 3·5 per cent and 5·9 per cent for Oil B. Various factors, as for example, the temperature at which the precipitated asphaltenes were washed with pentane, may account for the differences.

The maximum pour point of Oil A (see Fig 3) is 70° F after pretreatment at 100° to 110° F. Removal of asphaltenes gives a de-asphalted oil (pentane) with a pour point 10° to 25° F higher than the original oil, for pretreatment temperatures up to 110° F. At higher pretreatment temperatures there is a rapid drop in pour point, both oils giving a value around 15° to 20° F after pretreatment at 140° F. The pentane extract from alumina (Fraction 1 in Table III) has a very high pour point (about 75° F) which is relatively unaffected by the temperature of pretreatment. The acetone treatment of Fraction 1 gives two fractions, one insoluble, Fraction 1*a*, and the other soluble, Fraction 1*b*, in acetone. The pour points of both fractions are unaffected by the pretreatment temperature, the acetone-insoluble fraction having a pour point of 95° F and the acetone-soluble fraction a pour point of 50° F. Removal of 6·9 per cent of wax-like material, Fraction 1*a*(i), through the formation of a complex with urea, from the acetone-insoluble fraction lowers the pour point of the Fraction 1*a*(ii), from 95° to 80° F; similarly, the removal of 8·4 per cent of wax-like material, Fraction 1*b*(i), from the acetone-soluble fraction lowers the pour point from 50° to 20° F. Treatment of the acetone-insoluble material, after removal of the urea complex, that is Fraction 1*a*(ii), with methyl ethyl ketone, gives 4·2 per cent of wax, Fraction 1*a*(ii)A, and 95·8 per cent of material soluble in methyl ethyl ketone, Fraction 1*a*(ii)B, having a pour point of 70° F, so that the removal of 4·2 per cent of methyl-ethyl-ketone-insoluble wax lowered the pour point 10° F. The final treatment of Fraction 1*a*(ii)B with acetone–methylene chloride gives 30·6 per cent of insoluble material, Fraction 1*a*(ii)B_1, and 68·2 per cent of soluble material, Fraction 1*a*(ii)B_2. This latter fraction has a pour point of 60° F, 10° F lower than Fraction 1*a*(ii)B.

The pour point of Oil B is unaffected by the pretreatment temperature up to 130° F, but falls from 50° F after pretreatment at this temperature to 30° F after pretreatment at 170° F (see Fig 4). For pretreatment

TABLE III

Separation of Oil A into Various Fractions

Fraction	Per cent based on		Ultimate analysis, per cent						Molecular weight *	Atomic ratio, H/C	Refractive index, n_D^{20}	Asphaltenes,† per cent	Wax,‡ per cent
	Fraction taken	Original oil	Carbon	Hydrogen	Nitrogen	Sulphur	Diff	Ash					
Original oil	100	100	84·85	11·85	0·2	3·1	Nil	0·02	397	1·673	—	2·8	10·3
Asphaltenes	—	4·5	81·2	8·5	0·86	8·7	0·3	0·44	1970	1·220	—	—	—
Deasphalted oil (pentane)	—	95·5	83·9	11·8	0·25	2·4	1·65	Nil	403	1·665	—	0·5	10·3
Extracts from Alumina :													
1. Pentane extract	80·7	89·4	84·9	12·5	0·21	1·9	0·49	Nil	380	1·736	1·5061	0·1	15·9
2. Benzene extract	8·1	9·0	82·3	8·9	1·16	6·03	1·61	Nil	1267	1·297	—	—	—
3. Benzene–alcohol extract	1·4	1·6	78·5	9·2	0·9	6·7	4·1	0·6	1342	1·406	—	—	—
Not extracted and loss	9·8	—	—										
Total	100	95·5											
1. *Pentane Extract from Alumina :*													
(*a*) Insoluble in acetone	54·9	48·5	85·1	12·8	0·17	1·83	0·10	Nil	446	1·806	1·499	0·2	23·4
(*b*) Soluble in acetone	42·0	37·0	85·0	11·6	0·22	2·15	1·03	Nil	315	1·636	1·517	0·2	5·8
Loss	3·1	—	—										
Total	100	85·5											
1a. *Pentane Extract from Alumina—Fraction Insoluble in Acetone :*													
(i) Fraction forming urea complex	6·6	3·4	84·2	14·1	—	—	—	—	372	2·01	1·486	—	—
(ii) Fraction not forming urea complex	89·3	45·1	85·4	12·6	—	1·8	—	—	426	1·77	1·504	—	—
Loss	4·1	—	—										
Total	100	48·5											
1b. *Pentane Extract from Alumina—Fraction Soluble in Acetone :*													
(i) Fraction forming urea complex	8·3	3·1	84·9	13·3	—	—	—	—	308	1·879	1·4814	—	—
(ii) Fraction not forming urea complex	90·3	33·9	84·9	11·2	—	2·12	—	—	326	1·582	1·5212	—	—
Loss	1·4	—	—										
Total	100	37·0											
1a (ii). *Acetone Insoluble—Fraction not Forming Urea Complex :*													
(A) Insoluble in methyl ethyl ketone	4·1	1·9	85·2	13·5	—	—	—	—	528	1·846	1·5212	—	—
(B) Soluble in methyl ethyl ketone	94·7	43·2	85·5	12·6	—	—	—	—	428	1·767	1·5001	—	—
Loss	1·2	—	—										
Total	100	45·1											
1a (ii) B. *Fraction Soluble in Methyl Ethyl Ketone :*													
a (ii) B_1. Insoluble in acetone–methylene chloride (4 : 1)	30·0	13·2	85·15	12·6	—	—	—	—	601	1·770	1·5025	—	—
a (ii) B_2. Soluble in acetone–methylene chloride (4 : 1)	68·2	30·0	84·7	12·6	—	—	—	—	406	1·785	1·4992	—	—
Loss	1·8	—	—										
Total	100	43·2											

* Molecular weight—by the elevation of the boiling point of benzene. † Asphaltenes—according to IP 6/49. ‡ Wax—material insoluble in methylene chloride at −25° F

TABLE IV

Separation of Oil B into Various Fractions

Fraction	Per cent based on			Ultimate analysis, per cent						Molecular weight *	Atomic ratio, H/C	Refractive index, n_D^{20}	Asphaltenes,† per cent	Wax ‡ per cent
	Fraction taken		Original oil	Carbon	Hydrogen	Nitrogen	Sulphur	Diff	Ash					
Original oil	100	100	100	84·55	11·35	0·3	3·8	Nil	0·02	539	1·613	—	2·1	9·5
Asphaltenes	—	3·5	3·5	82·2	8·4	0·7	6·9	1·5	0·3	1498	1·228	—	—	—
Deasphalted oil (pentane)	—	96·5	96·5	84·5	11·4	—	—	—	—	488	1·619	—	0·5	10·1
Extracts from Alumina:														
1. Pentane extract	80·0	83·7	80·8	84·4	11·5	—	—	—	—	460	1·634	1·5227	Trace	10·3
2. Benzene extract	9·5	9·9	9·5	—	—	—	—	—	—	—	—	—	—	—
3. Benzene–alcohol extract	6·1	6·4	6·2	—	—	—	—	—	—	—	—	—	—	—
Not extracted and loss	4·4	—	—	—	—	—	—	—	—	—	—	—	—	—
Total	100	100	96·5											
1. *Pentane Extract from Alumina:*														
(*a*) Insoluble in acetone	32·4	32·7	26·4	84·2	12·2	—	—	—	—	764	1·739	1·5189	0·6	16·5
(*b*) Soluble in acetone	66·6	67·3	54·4	84·2	11·4	—	—	—	—	370	1·624	1·5248	Trace	5·4
Loss	1·0	—	—											
Total	100	100	80·8											
1*a*. *Pentane Extract from Alumina—Fraction Insoluble in Acetone:*														
(i) Fraction forming urea complex	3·0	3·0	0·8	—	—	—	—	—	—	—	—	—	—	—
(ii) Fraction not forming urea complex	97·0	97·0	25·6	83·6	12·2	—	—	—	—	707	1·751	1·5190	—	—
Loss	—	—	—											
Total	100	100	100											
1*b*. *Pentane Extract from Alumina—Fraction Soluble in Acetone:*														
(i) Fraction forming urea complex	6·2	6·3	3·4	—	—	—	—	—	—	398	—	1·4808	—	—
(ii) Fraction not forming urea complex	91·9	93·7	51·0	83·4	11·4	—	—	—	—	352	1·640	1·5293	—	—
Loss	1·9	—	—											
Total	100	100	54·4											
1*a* (ii). *Acetone Insoluble—Fraction not Forming Urea Complex:*														
(A) Insoluble in methyl ethyl ketone	23·3	23·3	6·0	82·1	12·0	—	—	—	—	1078	1·752	—	—	—
(B) Soluble in methyl ethyl ketone	76·7	76·7	19·6	83·9	12·2	—	—	—	—	814	1·742	1·5153	—	—
Loss	—	—	—											
Total	100	100	25·6											

* Molecular weight—by the elevation of the boiling point of benzene. † Asphaltenes—according to IP 6/49. ‡ Wax—material insoluble in methylene chloride at −25° F.

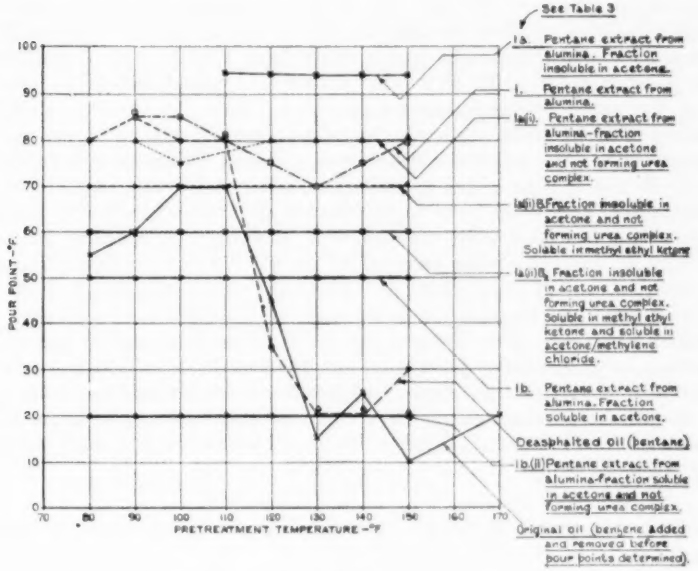

FIG 3

POUR POINT V HEAT PRETREATMENT TEMPERATURE FOR OIL A AND THE VARIOUS FRACTIONS OBTAINED FROM OIL A

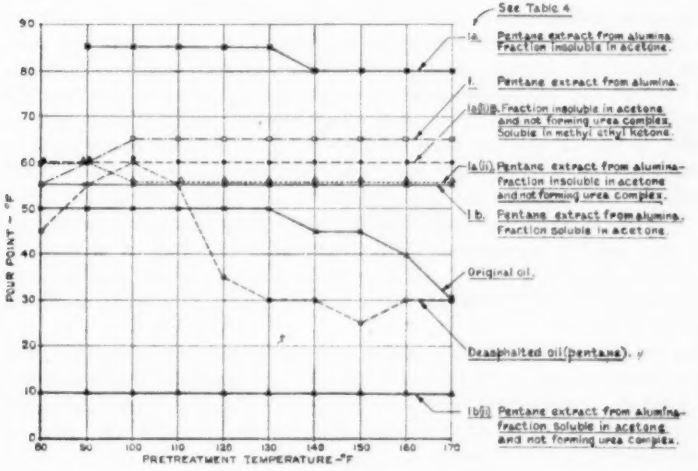

FIG 4

POUR POINT V HEAT PRETREATMENT TEMPERATURE FOR OIL B AND THE VARIOUS FRACTIONS OBTAINED FROM OIL B

temperatures between 85° and 110° F, the de-asphalted oil (pentane) has a higher pour point than the original oil, the maximum value being 60° F. Increasing the pretreatment temperature from 110° to 130° F lowers the pour point from 55° to 30° F, a value considerably below that of the original oil at the same pretreatment temperature. Thus, in the case of Oil B removal of asphaltenes has made the oil more sensitive to the pretreatment temperature. The pentane extract from alumina (Fraction 1 in Table IV) of Oil B has a pour point relatively unaffected by the temperature of pretreatment and about 10° F higher than that of the original oil. Fraction 1 gives two fractions when treated with acetone, the insoluble material, Fraction 1*a*, having a pour point of 80° to 85° F and the soluble material, Fraction 1*b*, a pour point of 55° F. Removal of the straight-chain hydrocarbons from the acetone–insoluble material through the formation of a complex with urea, gives 3·0 per cent of Fraction 1*a*(i) and 97 per cent of Fraction 1*a*(ii), the latter having a pour point of 55° F so that the removal of 3·0 per cent of straight-chain hydrocarbons has lowered the pour point 25° to 30° F. In the case of the acetone-soluble fraction, removal of 6·3 per cent of straight-chain hydrocarbons, Fraction 1*b*(i), lowers the pour point from 55° to 10° F.

Rheological Properties of Oil A, Deasphalted (pentane) Oil A and the Pentane Extract from Alumina

Pour Point. The pour points of the three oils now considered have already been described above, and are plotted against the heat pretreatment temperature in Fig 3.

Viscometric Data. The breakdown of the original Oil A was studied at a constant rate of shear (13·18 sec^{-1}) in a coni-cylindrical viscometer at 52° F, after pretreatment at various temperatures between 80° and 140° F. The results are given in Fig 5, from which it is clear that the shearing stress is initially high for the oils pretreated at temperatures between 80° and 110° F, *i.e.*, at temperatures giving the high pour points (see Fig 3); 2½ to 3 hours are required to reach equilibrium. With the oils pretreated at 120° to 140° F (*i.e.*, at temperatures giving low pour points) the initial shearing stress is relatively low, and equilibrium is reached within 20 minutes. The equilibrium shearing stress at 52° F was then studied for Oil A in both low- and high-fluidity conditions (samples pretreated at 100° and 140° F respectively), at three different rates of shear, namely 1·05, 6·02, and 13·18 sec^{-1}. These data, together with similar data for the deasphalted oil (pentane) and the pentane extract from alumina, are given in Fig 6.

The breakdown of the deasphalted (pentane) Oil A was studied at 52° F and a rate of shear of 13·18 sec^{-1}, but only for samples preheated to 100° and 140° F. These data, given in Fig 7, show that the time necessary to achieve equilibrium is much the same as for the original oil. The equilibrium shearing stress however, is, only 240 dynes/cm^2 for the oil preheated at 100° F compared to 500 dynes/cm^2 for original Oil A; the comparison for oils preheated at 140° F is between 105 and 120 dynes/cm^2.

Similar data to those obtained for the deasphalted oil were also obtained for the pentane extract from alumina. Samples were tested after pre-

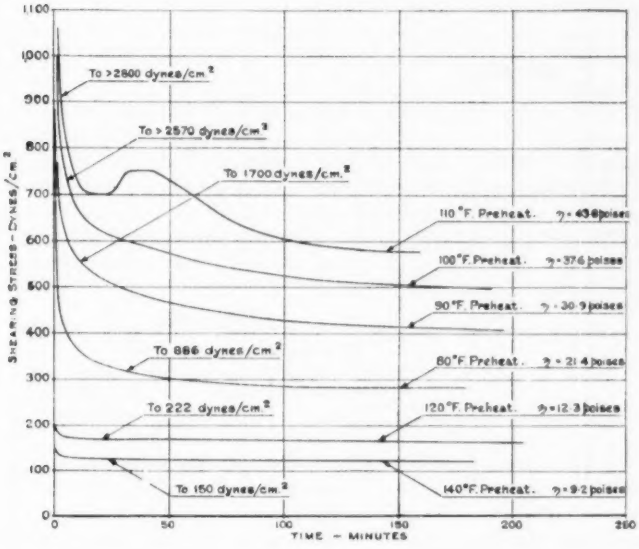

FIG 5

OIL A AFTER PREHEATING AT VARIOUS TEMPERATURES VARIATION OF SHEARING STRESS WITH TIME AT CONSTANT RATE OF SHEAR (13·18 SEC^{-1})

Determinations at 52° F

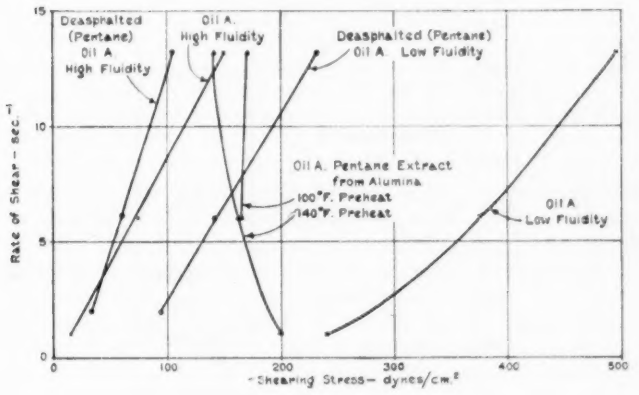
Deasphalted (Pentane) Oil A High Fluidity
Oil A. High Fluidity
Deasphalted (Pentane) Oil A. Low Fluidity
Oil A. Pentane Extract from Alumina
100°F. Preheat
140°F. Preheat
Oil A. Low Fluidity
Rate of Shear - Sec.⁻¹
- Shearing Stress - dynes/cm.²

FIG 6

OIL A AND DEASPHALTED (PENTANE) OIL A IN HIGH- AND LOW-FLUIDITY CONDITION AND PENTANE EXTRACT FROM ALUMINA (100° F AND 140° F PREHEAT)

Rate of shear v shearing stress at equilibrium at 52° F

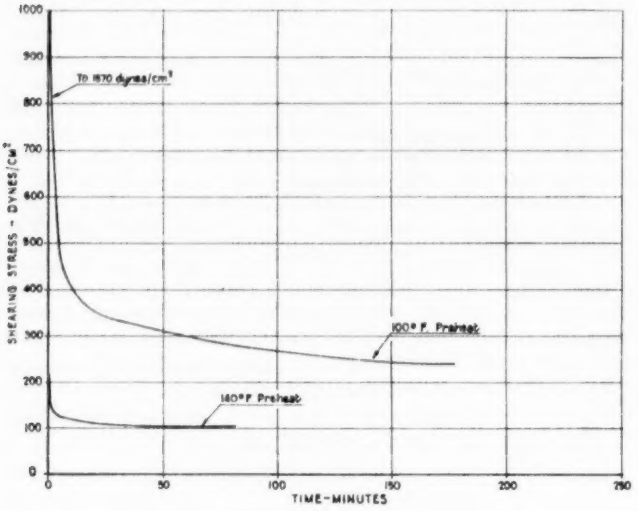

FIG 7

DEASPHALTED (PENTANE) OIL A. VARIATION OF SHEARING STRESS WITH TIME AT CONSTANT RATE OF SHEAR (13·18 SEC^{-1})

Determinations carried out at 52° F

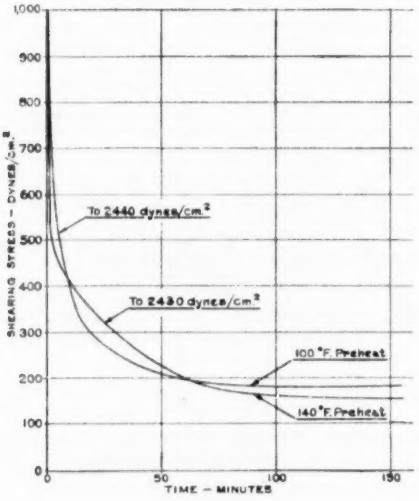

FIG 8

OIL A. PENTANE EXTRACT FROM ALUMINA. VARIATION OF SHEARING STRESS WITH TIME AT CONSTANT RATE OF SHEAR (13·18 SEC^{-1})

Determination carried out at 52° F

treatment at 100° and 140° F, although the pour point data had already shown that this fraction is relatively insensitive to the temperature of pretreatment. The manner in which the shearing stress falls with time at a constant rate of shear (13·18 sec^{-1}) is shown in Fig 8. The equilibrium value is obtained in about 1½ hours, and is practically the same for the two samples (150 to 180 dynes/cm^2).

The behaviour of the three oils, when the rate of shear is progressively lowered after the equilibrium shearing stress has been reached at 13·18 sec^{-1}, is of interest. These data are presented in Fig 9. In every case the complete curve was obtained within 30 to 40 minutes of the equilibrium shearing stress at 13·18 sec^{-1} having been achieved.

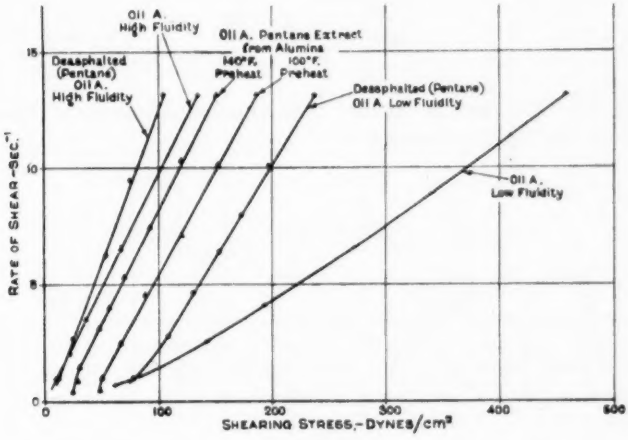

FIG 9

OIL A AND DEASPHALTED (PENTANE) OIL A IN HIGH- AND LOW-FLUIDITY CONDITION AND PENTANE EXTRACT FROM ALUMINA

100° F and 140° F preheat. Rate of shear *v* shearing stress. Initial breakdown at 13·18 sec^{-1}. Temperature 52° F

Yield Values. The yield values of the three oils were measured by means of a modified form of the IP setting point apparatus, designed by the Research Staff of the Anglo-Iranian Oil Co. Ltd., and in all cases determinations were made at 32° F. The data obtained are given in Table V.

Comparison of Data. The effect of pretreatment temperature on rheological properties was studied over the whole range from 70° to 140° F only in the case of original Oil A. In Fig 10 the pour point, the equilibrium viscosity, and the yield value have been plotted against the pretreatment temperature. Each of these properties reaches a maximum value after pretreatment at temperatures between 90° and 110° F, and falls away to a more or less steady value at a temperature of roughly 140° F. The deasphalted oil (pentane) shows a similar sensitivity towards the pretreatment temperature, but complete data were obtained only for pour

TABLE V

Yield Values of Oil A, Deasphalted (pentane) Oil A and the Pentane Extract from Alumina

Heat pretreatment temperature, ° F	Yield values at 32° F, dynes/cm²		
	Oil A	Deasphalted (pentane) Oil A	Pentane extract from alumina
70	760	—	—
80	1250	170	—
90	1430	—	370
100	1350	470	430
110	1190	—	—
120	640	60	500
130	40	—	—
140	120	60	—
150	30	—	—

point (Fig 3). The pentane extract from alumina is relatively insensitive to the temperature of pretreatment.

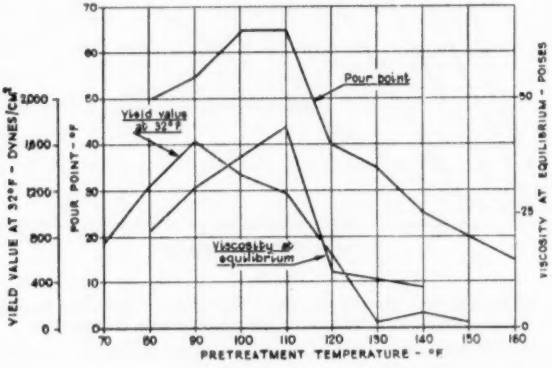
Pour point
Yield value at 32°F
Viscosity at equilibrium
YIELD VALUE AT 32°F - DYNES/CM²
POUR POINT - °F
VISCOSITY AT EQUILIBRIUM - POISES
PRETREATMENT TEMPERATURE - °F

FIG 10

OIL A. COMPARISON OF POUR POINT, VISCOSITY, AND YIELD VALUE DATA (MEASURED AT 52° F)

Variation with heat pretreatment temperature.

In Table VI a comparison is made of the pour points, the initial and equilibrium viscosities, and yield value for the three oils, after pretreatment at 100° and 140° F respectively. Considering first the oils in the condition of low fluidity (pretreatment at 100° F), it is seen that the pentane extract from alumina has a pour point of 85° F, the deasphalted (pentane) Oil A, 80° F, and Oil A, 70° F. In contrast, the initial viscosity, the equilibrium viscosity, and the yield value of Oil A are higher than the corresponding values for the deasphalted oil or for the pentane extract. On the other hand, the deasphalted oil and the pentane extract do not differ greatly in the rheological properties shown after pretreatment at 100° F, though this is no longer true after pretreatment at 140° F. Pretreatment at this

temperature hardly alters the properties of the pentane extract, but drastically reduces the pour point, the yield value, and the viscosity of both the original Oil A and the deasphalted (pentane) Oil A.

The deasphalted oil (pentane) was prepared from the original oil by the removal of 4·5 per cent of asphaltenes, and the pentane extract from

TABLE VI

Comparison of Pour Point, Viscosity, and Yield Value

Type of oil	Oil A	Deasphalted (pentane) Oil A	Pentane extract from alumina
Condition of oil	Low fluidity (*i.e.*, 100° F pretreatment)		
Pour point, ° F	70	80	85
Initial viscosity, poises *	195	119	185
Equilibrium viscosity, poises *	38	18	14
Yield value at 32° F, dynes/cm²	1350	470	430
Condition of oil	High fluidity (*i.e.*, 140° F pretreatment)		
Pour point, ° F	25	20	75
Initial viscosity, poises *	11·4	11·4	184
Equilibrium viscosity, poises *	9·2	8·0	10·8
Yield value at 32° F, dynes/cm²	120	60	500 (120° F pretreatment)

* Viscosities measured at 52° F and 13·18 sec^{-1}.

alumina was prepared from the deasphalted oil by the removal of 10 per cent of resins. It is therefore apparent from the changes brought about by different heat pretreatments that the asphaltenes and the resins both have a powerful effect in reducing the pour point and the yield value. There is, however, a difference in the action of these two substances, which is evident from the data for the three oils in the low-fluidity condition. Here the presence of the asphaltenes is seen to make a large difference between the properties of the original oil and the deasphalted oil (pentane), but the presence of the resins apparently makes little difference between the deasphalted oil and the pentane extract. It is in fact clear from the viscometric and yield value data that the structure of the original oil is greatly strengthened by the asphaltenes, acting alone or in conjunction with the resins, in spite of the fact that the pour point is reduced. The resins alone, however, do not appear to contribute appreciably to the structure of the deasphalted oil in the condition of low fluidity.

The data in Figs 5, 7, and 8 showing the breakdown of the oils with time at constant rate of shear, indicate no marked differences in the general behaviour of the original oil, the deasphalted oil (pentane) (both in the low fluidity condition), and the pentane extract. Each contains some structure which is progressively degraded until equilibrium is reached. In the high fluidity condition the two former oils appear to possess only slight structure.

The data in Fig 6, in which the shearing stress at equilibrium has been plotted against the rate of shear, show considerable differences between the oils. Thus, the shape of the curve for the original oil in the condition of low fluidity indicates that the oil possesses anomalous viscous properties,

and extrapolation to zero rate of shear would suggest that the existence of a yield value is at least doubtful. The deasphalted oil in the condition of low fluidity has a definite yield value, and so must possess some structural factor not found in the original oil. The pentane extract shows a peculiar behaviour; when it is pretreated at 140° F the shearing stress at equilibrium increases as the rate of shear decreases, and when it is pretreated at 100° F the equilibrium shearing stress is hardly affected by change in the rate of shear. Extrapolation to zero rate of shear shows the pentane extract to possess a pronounced yield value. No theory can yet be advanced to explain how the resultant shearing stress can decrease with increasing rate of shear, but the phenomenon indicates the complicated nature of the structure.

The data in Fig 9, showing the effect of progressively lowering the rate of shear after the equilibrium shearing stress has been obtained at a rate of shear of 13·18 sec^{-1}, lead to conclusions very similar to those drawn from Fig 6. The original oil and the deasphalted oil in the condition of low fluidity are similar in possessing anomalous viscous characteristics, but differ in that only the latter has a yield value; when the oils are in the condition of high fluidity their behaviour is almost Newtonian. The pentane extract, after treatment both at 100° and 140° F, shows the existence of a yield value, and at a rate of shear of about 1·0 sec^{-1} the curve undergoes a change in slope, indicating a change in the structure of the system.

Microscopical Examination

Oil A

Plate I shows photomicrographs of Oil A after pretreatment at various temperatures. All the photographs were taken at room temperature. In the samples treated at temperatures of 90° to 110° F crystalline wax could not be detected, even when the examination was made with polarized light, and it must be concluded either that all the wax is in solution or that it has separated as crystals too minute (less than 1 μ) to be detected by the microscope. With progressive increase in the pretreatment temperature, larger wax crystals separate out and aggregation occurs, the size of the aggregates increasing as the pretreatment temperature is raised to 140° F; the largest are in the region of 20 to 30 μ.

In Plate II*a*, X-ray diffraction patterns are given of Oil A in the low- and high-fluidity conditions (pretreatment temperatures of 100° and 140° F respectively). The two patterns are practically identical. As determined by solubility in methylene chloride this oil contains 10·3 per cent of wax. A sample rich in wax was prepared by filtering the original oil in the high-fluidity condition, until the residue contained 30 per cent of wax (by the methylene chloride method) and the filtrate 10 per cent of wax. The residue amounted to 8 per cent and the filtrate 92 per cent of the original oil. The total wax in the residue plus filtrate thus amounts to 11·6 per cent, compared to 10·3 per cent in the original oil. The apparent gain in wax content on filtration may be due to the empirical nature of the methylene chloride method for the determination of wax. In Plate II*c* the X-ray diffraction pattern is given of the residue, and in Plate II*d*

that of the filtrate which is free from crystalline wax. In Plate II*b* X-ray diffraction patterns are given of a mixture of 85 per cent of original Oil A, and 15 per cent of the residue, in both low- and high-fluidity conditions. This plate shows rather more clearly than Plate II*a* the diffraction ring due to the presence of crystalline wax (cf. Plate II*c*) and the similarity between the low- and high-fluidity conditions. The X-ray diffraction pattern of the filtrate, Plate II*d*, is given so that Plates II*a* and *b* may be compared with an oil free from crystalline wax. It is concluded that the original oil in the low-fluidity condition contains crystalline wax, which is, moreover, approximately equal in amount to that in the oil in the high-fluidity condition.

It is evident that when the wax is present as a great number of small crystals (low-fluidity condition) it has a powerful effect on the viscous properties of the oil; but when present as a relatively small number of large aggregates (high-fluidity condition) it has little effect on the viscous properties of the oil.

Plates III*a*, III*b*, and III*c* are photomicrographs of the pentane extract from alumina of Oil A taken at room temperature after pretreatment at 70°, 100°, and 140° F respectively. This fraction represents 85·5 per cent of the original oil, and differs from the original oil in being free from asphaltenes and resins. After pretreatment at 70° F the fraction is seen to contain needle-shaped crystals, though these are small, rather ill-defined, and difficult to detect even under high magnification. Pretreating at 100° F results in the formation of much more well-defined needles, but they do not appear to be much larger than those obtained after pretreatment at 70° F. Pretreating at 140° F results in the formation of considerably larger needle-shaped crystals. It would appear that pretreatment at 70° F results in the formation either of some crystals too small to be seen under the microscope or possibly of a supersaturated solution of wax.

A sample of Oil A, in the high-fluidity condition, was filtered through a metal sinter of pore size 2 to 5 μ in order to remove the large crystal aggregates. The filtrate was then adsorbed on alumina, and subsequently extracted with pentane. On examination of this extract under the microscope (photomicrographs not recorded) whatever the pretreatment, no wax crystals could be detected. It is therefore evident that the crystal aggregates seen in the original oil in the high-fluidity condition, and the needle-shaped crystals present in the pentane extract from alumina, are composed of the same waxes.

The contrasting behaviour of Oil A in conditions of low and high fluidity as it is cooled to −4° F is illustrated by Plates IV and V respectively. At room temperature (69° F) the oil of low fluidity shows no granular material; on cooling to 41° F granular material begins to be noticeable, and becomes progressively more pronounced as the temperature falls through 32° F and 14° F to −4° F. At room temperature the oil of high fluidity shows a considerable number of wax crystals in the form of large aggregates; on cooling to −4° F these large aggregates are unchanged, but a secondary deposit of very small crystals separates. In both cases the oil returns to its original state when the temperature rises to room temperature.

A series of photomicrographs similar to that given in Plate I for Oil A was prepared for the deasphalted oil (pentane) from Oil A. In all respects

this series duplicated that for the original oil, and it must therefore be concluded that the presence of the asphaltenes precipitated by pentane is not essential for the formation of large wax aggregates in the high-fluidity condition.

Oil B

When photomicrographs of Oil B were taken, after pretreatment at various temperatures, there was complete absence of any visible crystalline material until a pretreatment temperature of 160° F was reached; a small amount of rather small, isolated, needle-shaped crystals was then observed. After the asphaltenes had been removed from this oil by treatment with pentane, wax crystals formed more readily than in the original oil; crystals

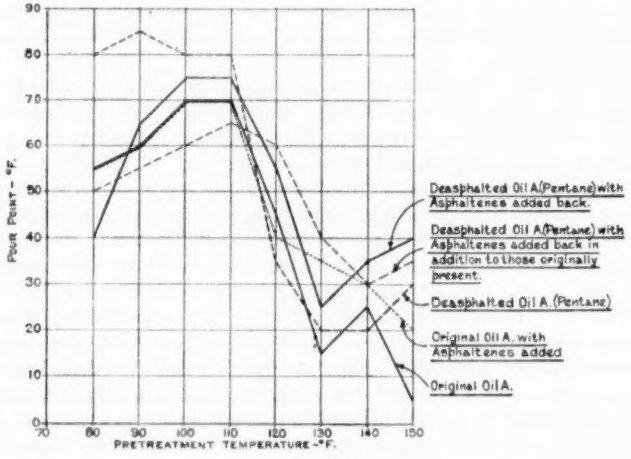

FIG 11

ADDITION OF ASPHALTENES TO OIL A

first appeared at a pretreatment temperature of 140° F, and on pretreating at 160° F they appeared as moderately large and well-defined aggregates. This difference between the original oil and the deasphalted oil (pentane) is in agreement with the pour point data given in Fig 4, from which it is seen that the latter oil is more sensitive than the former to the pretreatment temperature.

Reconstitution of Oil A from its Individual Fractions

In the work described in this paper, an important object was to throw some light, if possible, on the viscous properties of a fuel oil by examining the properties of fractions of the oil. It was thus essential that the separation of the oil into fractions should be made without altering the oil constituents in an irreversible manner; and it was important to determine whether Oil A could be reconstituted from its various fractions.

Fig 11 gives the pour points of a number of samples of reconstituted oils plotted against the temperatures to which the samples had been pre-

heated. Removal of asphaltenes results in a raising of the pour point for pretreatment temperatures up to 110° F. Both the deasphalted oil (pentane) and the original oil show pronounced heat sensitivity. When asphaltenes are added back to the deasphalted oil (pentane), equal in amount to those removed, the behaviour of the original oil is to a large extent reproduced, though the pour points of the reconstituted oil are somewhat higher than those of the original oil; the added asphaltenes are evidently not quite so effective as they were originally. When asphaltenes are added to the deasphalted oil in an amount in excess of that originally present in the oil (actually the amount was doubled), the pour point was lowered below that of the original oil, for pretreatment temperatures below 120° F; for higher pretreatment temperatures, the pour point was raised above that of the original oil. The addition of asphaltenes to the original oil had little effect for pretreatment temperatures below 120° F, but at higher temperatures the effect was to raise the pour point to some extent.

These results demonstrated that an oil that has had the asphaltenes removed from it can be reconstituted so that the behaviour of the resulting oil is very close to that of the original oil.

The photomicrographs in Plate VI show the effect on the appearance of the oil under the microscope of the addition of the benzene extract, the benzene–alcohol extract from alumina, and of asphaltenes, to the pentane extract from alumina of Oil A. The original pentane extract is shown in Plate III. The two extracts and the asphaltenes were added separately and jointly to the pentane-soluble fraction in the same proportions as they were present in the original oil (see Table III). In each case the mixtures were pretreated at 70° and 140° F. The effect of the addition of these materials to the pentane extract (after pretreatment at 140° F) is to change the needle-shaped crystals originally present into a rectangular and altogether more compact shape; there was also a tendency for aggregation to occur, and this was most pronounced with the benzene–alcohol extract. The same effect was obtained by pretreating at 70° F, but here the crystals formed were much smaller and more difficult to see. When all the fractions of the oil were re-combined in the proportions in which they were originally present, the crystal behaviour of the original oil was reproduced to a large extent.

Summary and Conclusions

The results recorded in this paper conform with the widely accepted view that the anomalous behaviour of certain wax-containing oils is due largely to the formation by the wax of some kind of structure.

In an oil free from resins and asphaltenes, wax separating from the oil usually appears as small needle-shaped crystals. The size of the crystals is influenced by the heat pretreatment given to the oil, and conditions which tend to increase the size of the crystals also tend to increase the fluidity of the system.

The effect of heat pretreatment on such oils, however, is small in comparison with the effect on residual fuel oils, in which the presence of asphaltenes and resins greatly increases the temperature sensitivity of the

system. When a residual fuel oil is in a condition of high fluidity, some of the wax is present as relatively large crystal aggregates. As the heat treatment is modified so as to reduce the fluidity of the system, crystal aggregates become less prominent and eventually disappear entirely. The separating crystals diminish in size as the system becomes less fluid and may become sub-microscopic. X-ray diffraction studies provide good reasons for believing, however, that the rheological properties of systems in a condition of very low fluidity are to a large extent determined by the structure imposed on the system by a matrix of extremely small crystals.

Wax–Oil System free from Asphaltenes and Resins

The system under discussion is a wax–oil system in which both constituents consist mainly of hydrocarbons, though related compounds containing sulphur, nitrogen, and oxygen are also present. The properties of this system are well known, but are far from being fully understood. With certain waxes, the system has the properties of: (1) oil retention, giving rise to the difficulty of separating the wax by mechanical processing, and (2) rigidity, as studied in the present work.

(1) *Oil retention.*—It is recognized that a proportion of the oil would be immobilized by adsorption on the surface of the crystals, but it is doubtful whether adsorption can fully account for the difficulty of filtering certain waxes. It seems possible that this is due to capillary action between the wax crystals, though on this view it is difficult to account for the action of substances such as Paraflow.

(2) *Rigidity.*—That the system may possess considerable rigidity is illustrated by the data recorded in Fig 9 for the pentane extract from alumina of Oil A. The extract has a well-defined yield value, which evidently decreases as the heat pretreatment temperature is raised and the crystals increase in size.

The nature of the forces which hold the crystals in a rigid structure is obscure. Jones and Tyson [10] have suggested that they are lattice forces arising from crystals growing into each other. It seems doubtful, however, whether such a mechanical linkage is in fact formed, since on this view an oil after it has been sheared should presumably not have a yield value.

After the structure has yielded, the relationship between rate of shear and shearing stress shows a change in slope at a rate of shear of about 1 to 1·5 sec^{-1}, presumably due to a change of structure. It may be that at this rate of shear the wax crystals take on an ordered arrangement which undergoes no further modification as the rate of shear is increased.

Wax–Oil System with Asphaltenes and Resins

The original Oil A (an wax–oil system containing asphaltenes and resins) has a pour point of 70° F after pretreatment to bring it into a condition of low fluidity or it may be as low as −5° F after pretreatment giving a condition of high fluidity. When the oil is treated with activated earth and solvents to remove the asphaltenes and resins, the remaining oil, which amounts to 85·5 per cent of the original oil, has a pour point of 80° F and is relatively insensitive to heat treatment.

It is therefore clear that in an oil in the condition of high fluidity, the

effect of asphaltenes and resins is to reduce the rigidity of the system by causing the wax to separate in the form of relatively large aggregates (Plate I). To explain this phenomenon, Kolvoort [4] has suggested a mechanism similar to that put forward to explain the action of pour point depressants such as Paraflow. It is not, however, clear how this action is influenced by heat pretreatment.

When the original Oil A is in a condition of low fluidity, it might appear that the effect of the asphaltenes is still to reduce the rigidity of the system (though to a much smaller extent) since the pour point is 10° F lower than that of the system free from asphaltenes and resins. The same conclusion might also be drawn from the fact that the asphaltene- and resin-free oil has a well-defined yield value, while the original oil probably shears under the smallest applied stress. When, however, the viscous properties, and the yield values as determined in a capillary U-tube, are considered (see Table VI), it is found that the presence of asphaltenes and resins strengthens the structure of the original oil.

It may be that this result is that to be expected from the known effect of asphaltenes and resins in increasing the viscosity of the system. In this case the rheological properties of a residual fuel oil, such as Oil A, would result from the simple addition of the properties of a colloidal dispersion of asphaltenes with those of a rigid structure of wax crystals. It seems, however, that the possibility cannot be ruled out that the asphaltenes and wax crystals interact in some way to produce a more rigid structure than would be expected from a simple mixture.

It also seems possible that an important effect of heat pretreatment may be to influence the rate and extent of the micellar growth of the asphaltenes, and that the effect on wax crystal structure may be consequential.

Before any explanation of the action of asphaltenes and resins in an oil of low fluidity can be offered, therefore, further studies are necessary to define more precisely the nature of this action, and these are at present in progress.

Acknowledgments

The author's thanks are due to the Anglo-Iranian Oil Company Ltd., for the help they have given in supplying samples of residual oils and providing the basic data necessary for the construction of a coni-cylindrical viscometer.

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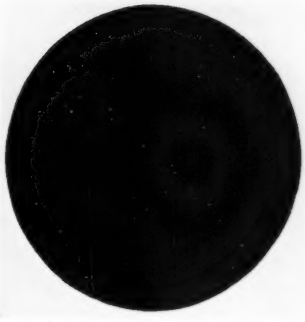
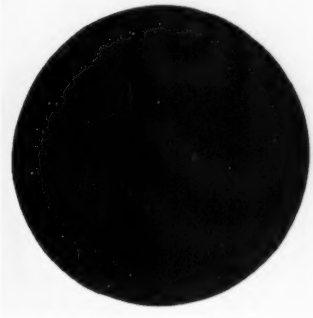


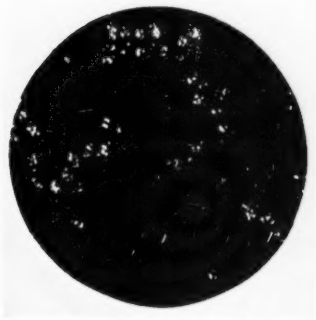
(*a*) Preheated to 100° F

(*b*) Preheated to 110° F

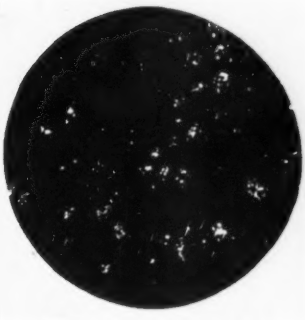


(*c*) Preheated to 115° F

(*d*) Preheated to 120° F



(*e*) Preheated to 130° F

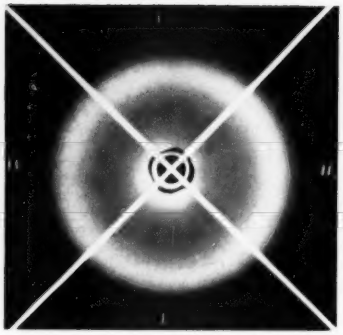


(*f*) Preheated to 140° F

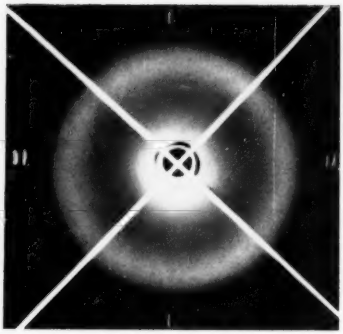
PLATE I

PHOTOMICROGRAPHS OF OIL A AFTER PRETREATMENT AT VARIOUS TEMPERATURES
(× 215)
Polarized light

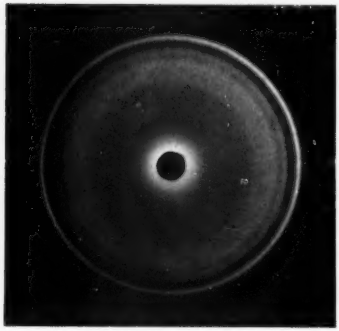
[*To face p.* 104.



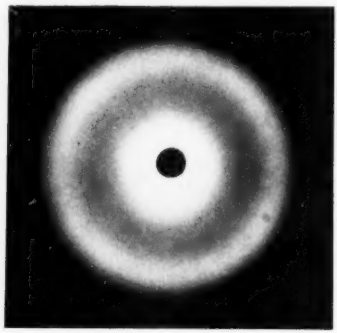
(*a*) Residual fuel oil in (ii) low- and (i) high-fluidity conditions



(*b*) Residual fuel oil with increased wax content in (ii) low- and (i) high-fluidity conditions



(*c*) Residual fuel oil containing 30 per cent wax (*i.e.*, residue from filtration of oil)

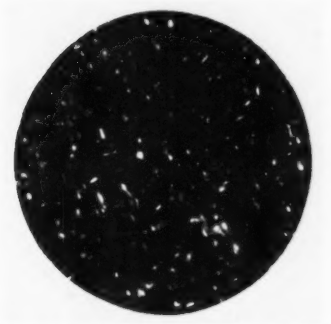


(*d*) Residual fuel oil after removal of crystalline wax by filtration.

PLATE II

X-RAY DIFFRACTION PATTERNS OF RESIDUAL FUEL OIL A

(*a*) Pretreatment temperature 70° F

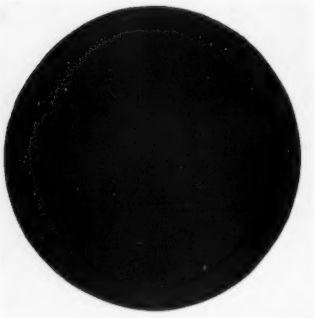


(*b*) Pretreatment temperature 100° F

(*c*) Pretreatment temperature 140° F

PLATE III

PHOTOMICROGRAPHS OF PENTANE EXTRACT OF OIL A FROM ALUMINA (× 215)
Polarized light



(*a*) At room temperature, 69° F

(*b*) Cooled to 41° F

(*c*) Cooled to 32° F

(*d*) Cooled to 14° F

(*e*) Cooled to −4° F

(*f*) Warmed to room temperature after cooling to −4° F

PLATE IV

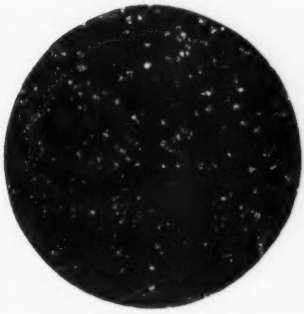
PHOTOMICROGRAPHS OF OIL A IN LOW-FLUIDITY CONDITION (× 48)

Polarized light. Effect of cooling to −4° F

(*a*) At room temperature—69° F

(*b*) Cooled to 41° F

(*c*) Cooled to 32° F



(*d*) Cooled to 14° F

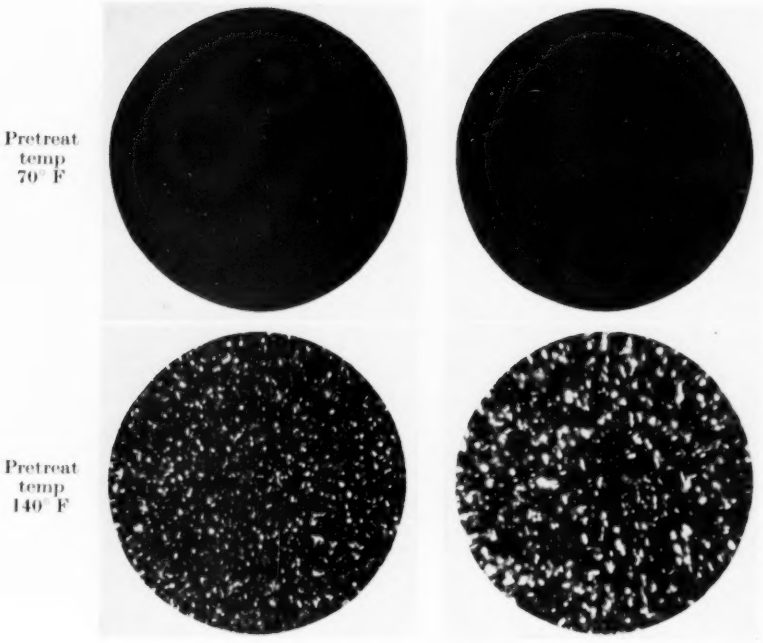
(*e*) Cooled to −4° F

(*f*) Warmed to room temperature after cooling to −4° F

PLATE V

PHOTOMICROGRAPHS OF OIL A IN HIGH-FLUIDITY CONDITION (× 48)

Polarized light. Effect of cooling to −4° F



A. 85·4 parts
B. 8·6 parts

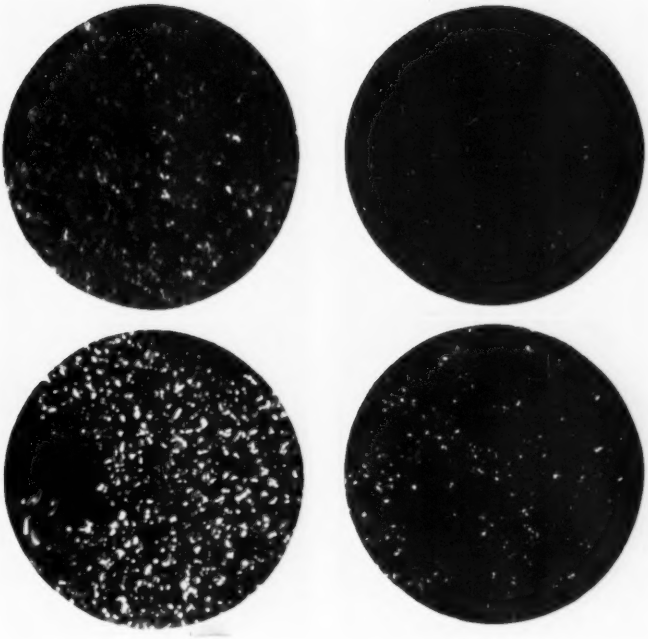
A. 85·4 parts
C. 1·5 parts

A. Pentane extract from alumina
B. Benzene extract from alumina
C. Benzene–alcohol extract from alumina
D. Asphaltenes (pentane)

PLATE VI

ADDITION OF VARIOUS EXTRACTS TO THE PENTANE EXTRACT OF OIL A FROM ALUMINA

Photomicrographs (× 215). Polarized light



Pretreat temp 70° F

Pretreat temp 140° F

A. 85·4 parts
D. 5·0 parts

A. 85·4 parts
B. 8·6 parts
C. 1·5 parts
D. 4·5 parts

PLATE VI (*continued*)

THE SOLUBILITY OF GASES IN LUBRICATING OILS AND FUELS

By R. R. Baldwin * † and S. G. Daniel * (Associate Fellow)

Summary

This paper describes briefly an apparatus devised for the measurement of the solubility of gases in oils, with particular reference to high viscosity oils. The results obtained with a series of solvent extracted oils derived from the same crude are presented and discussed, together with those obtained for a number of fuels. An attempt is made, with the aid of current solubility theories, to relate the observed results to other physical properties of the liquids.

Introduction

The dissolved gas content of a fuel or oil may, under certain circumstances, limit the range of operating conditions in which a fuel, lubricating oil, or hydraulic system will function satisfactorily. For example, the performance of a given fuel system in an aircraft is limited, at high altitudes, by excessive gas and vapour evolution in the pump. Tests on fuel systems have shown that, for a given system, the altitude at which this gas evolution occurs is determined by two factors, the vapour pressure of the fuel and the solubility coefficient of air in the fuel. The same two fuel properties also govern the occurrence of "vapour lock" in automobile fuel systems. In the case of oil, which has a negligible vapour pressure, the part played by air, whether dissolved or entrained, is clearly decisive. Despite these limitations which the dissolved gas content of petroleum fractions may impose upon the range of operating conditions of aircraft engines and other mechanical devices, relatively little information is available regarding the solubility of gases in the liquids used in these systems. Data relating to pure liquids are numerous, and the position has recently been summarized by Markham and Kobe,[1] but for the complex hydrocarbon mixtures derived from crude petroleum the published figures vary over a considerable range and are to some extent conflicting.[2–8] In the case of gasolines and kerosines, an accurate method for the determination of the solubility of gases has been devised recently by Glendinning and Bedwell,[9] and their results, together with those of earlier workers, enable the solubility of gases in current aviation fuel types to be estimated with some degree of certainty. For petroleum oils, however, there appears to be a general lack of accurate data for a range of oils of established characteristics, although it is evident that the origin, method and degree of refining, and viscosity exert a considerable influence upon gas solubility.[2, 5] In addition, the effect of temperature upon solubility appears uncertain, some workers reporting an increase with increasing temperature, and others a decrease both for air [3,5] and nitrogen.[4, 7, 8]

This paper records the results of gas solubility measurements made on a

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† Present address: University College, Hull.

series of petroleum fractions of different viscosities in an attempt to remedy the lack of accurate data and also attempts to relate the results to certain physical properties of the liquids examined.

Apparatus and Method of Measurement

The apparatus and method used to measure the solubility of gases in oils of negligible vapour pressure have been described in detail elsewhere,[10] and only a brief description will be given here. The method was designed

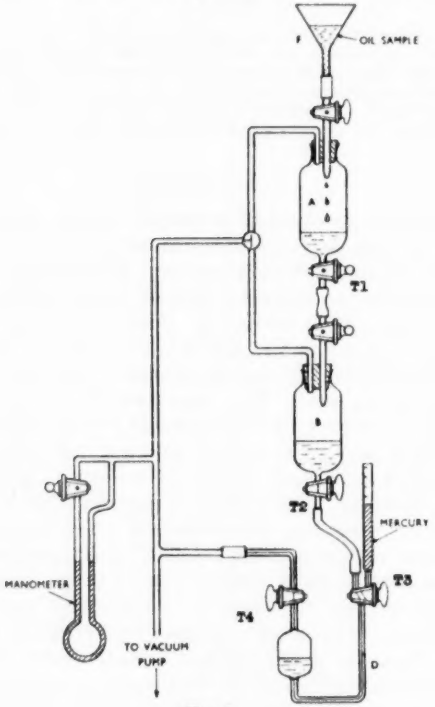

Fig 1

APPARATUS FOR THE DE-AERATION OF OILS OF NEGLIGIBLE VAPOUR PRESSURE

to overcome difficulties due to the high viscosity of some lubricating oils, and is therefore particularly suitable for use with viscous liquids, although with slight modifications it may be easily adapted for use with liquids (*e.g.*, gasolines and kerosines) of low viscosity and appreciable vapour pressure. The method consists essentially of two operations, first, the saturation of the liquid with the gas under examination, and secondly, determination of the amount of dissolved gas in the saturated liquid.

Saturation of the Oil Sample

The oil is first freed from any dissolved gas (usually air) by allowing it to stream into a continuously evacuated vessel, a convenient experimental arrangement being shown in Fig 1. Tests showed that even this drastic

treatment failed to remove all the dissolved gas, some 2 to 3 per cent remaining in solution; this observation illustrates the difficulty of operating with viscous liquids. To eliminate this residual air, the oil in *A* (Fig 1) is then given a preliminary saturation with the gas under examination before being allowed to stream into a second continuously evacuated vessel *B*. This procedure gives an oil which is practically free from the dissolved gas initially present, but which contains a small fraction of the gas under examination.

This oil is then transferred to a specially designed evacuated displacement burette *D* (Fig 1), the transference being accelerated in the case of oils of high viscosity by admitting the gas under examination into the vessel *B* at a pressure of about one atmosphere. When sufficient oil has entered the burette *D*, taps *T*3 and *T*4 are closed, the burette placed in a thermostat, and the gas under examination bubbled through the oil until saturation is complete. With viscous oils (above 800 cs at ambient temperatures), the time required for saturation is found to be about 5 hr, with less viscous oils (below 400 cs at ambient temperatures) 2 hr is sufficient, while with kerosine and gasoline only a short period of vigorous agitation is necessary. To check that saturation is complete, more gas is passed through the liquid remaining in the burette after the solubility determination and a second determination have been carried out. If the two determinations agree to within 1 per cent, the oil is considered to be saturated, and the mean value is taken as the solubility of the gas in the oil. When saturation is judged complete, the taps of the burette are closed and the oil allowed to stand until all gas bubbles have settled out (a process which may require up to 1 hr with very viscous oils). The gas above the oil in the burette is then displaced by admitting mercury from the graduated tube above *T*3, and tap *T*4 closed, *T*3 being left open with a head of some 10 cm of mercury to keep the gas in solution during storage prior to test.

Determination of the Dissolved Gas Content

To determine the dissolved gas content of the sample, the displacement burette is connected to the apparatus shown in Fig 2. It consists essentially of a vessel *V* connected by a ground glass joint to a Töpler pump *P*, a manometer *M*, and a calibrated volume *S*. The apparatus is first evacuated to a pressure of 10^{-3} mm Hg or better, and a suitable volume of oil (about 10 ml) is allowed to enter vessel *V*, which is heated to 150° C to facilitate the release of dissolved gas. The change in mercury level in the graduated arm of the burette gives an accurate measure (to within $\pm 0{\cdot}02$ ml) of the amount of oil introduced, and the positive displacement of the oil eliminates errors due to drainage. The released gas is drawn through a trap *T*, maintained at −80° C to remove any traces of oil vapour, and compressed into the bulb *S* by means of the Töpler pump, four or five strokes of the pump being sufficient to collect all the gas, provided the volume of vessel *V* and trap *T* are kept reasonably small. In most cases a small amount of gas will remain in solution in the oil, and this may be released by gently heating the oil until it boils under the vacuum in the apparatus. This gas (up to 5 per cent of the total figure) is also collected in vessel *S* by the Töpler pump. A figure greater than 5 per cent should be regarded with some suspicion, as it may indicate cracking of the oil.

The amount of gas collected in the vessel S is then determined by measuring the pressure it exerts in a known volume. The tap $T8$ is turned so that the Töpler pump is connected to vessel S and the mercury level brought to a fixed mark L. The mercury level in the manometer M is noted, and on subtracting this reading from that obtained by a similar procedure when

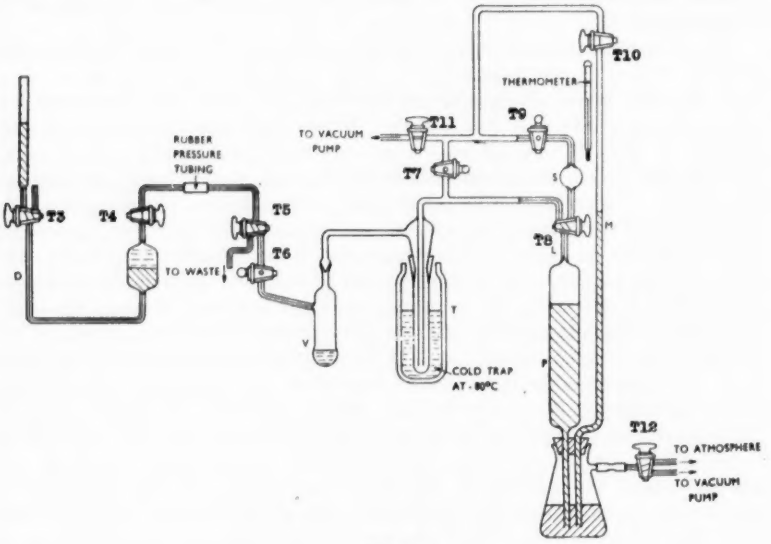

FIG 2

APPARATUS FOR THE DETERMINATION OF THE DISSOLVED GAS CONTENT OF OILS AND FUELS

S is completely evacuated, the pressure exerted by the gas is obtained. The volume of gas at N.T.P. obtained from the sample is given by :—

$$p.v.\ 273{\cdot}2/760\ T \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p, v, and T are the pressure, volume, and absolute temperature of the collected gas respectively. The Bunsen solubility coefficient α_v is given by :—

$$\alpha_v = p.v.\ 273{\cdot}2/P_a.\ V.\ T \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where V is the volume of oil used and P_a the atmospheric pressure at which the oil was saturated.

The experimental error, estimated at about ± 1 per cent, is largely determined by the pressure readings, which, owing to sticking of the mercury manometer in the relatively small bore (4 mm) tubing, may introduce an error of about 0·5 mm in the pressure difference recorded. The lowest pressure measured was about 50 mm Hg, so that an error of 1 per cent may arise, although in most cases the pressures were greater than 100 mm Hg.

and the error will be smaller. Greater accuracy could be obtained either by using a smaller calibrated vessel S or a suitable glass Bourdon gauge.

Modifications for Use with Liquids of Appreciable Vapour Pressure

For oils or fuels of appreciable vapour pressure, the apparatus shown in Fig 1 is unsuitable, and several modifications are necessary to prevent appreciable loss of lighter fractions. The removal of initially dissolved gas is carried out in the displacement burette D, which is cooled in a bath at $-80°$ C and evacuated. The liquid is slowly admitted through tap $T3$, and the liberated air is removed by momentarily opening tap $T4$ to the vacuum pump. The burette and contents are then warmed to room temperature, shaken vigorously, and cooled again to $-80°$ C. Any further released gas is again removed by momentarily opening $T4$ to vacuum. Five or six repetitions of this process are sufficient to remove all dissolved gas without any significant loss of volatile fractions. The burette is now immersed in a thermostat at the required temperature, the saturating gas admitted through $T3$ and released to atmospheric pressure through $T4$. Several shakings are sufficient to give saturation and the sample is then sealed off as before. This procedure avoids any loss of volatile fractions which would otherwise result if a large quantity of the saturating gas were bubbled through the liquid.

The actual solubility determination requires similar modification. Vessel V must be cooled to $-80°$ C, and trap T may require cooling with liquid air intead of cooling to $-80°$ C if the liquid is fairly volatile (*e.g.*, with 100-octane fuel). The final boiling under vacuum is unnecessary, as sufficient agitation can be provided by tapping V to effect the release of all the dissolved gas. The calculation of the Bunsen coefficient requires a knowledge of the vapour pressure of the liquid at the saturating temperature, and equation (2) becomes :—

$$\alpha_v = p.\, v\, 273{\cdot}2/(P_a - P_L)V.T. \quad . \quad . \quad . \quad . \quad (3)$$

where P_L is the vapour pressure of the liquid at the temperature at saturation. In the calculation of the solubility coefficient, Henry's Law has been assumed to hold over the pressure range involved; evidence for this has been provided by various workers.[3, 4, 6]

The oxygen, nitrogen, and hydrogen used in the determinations were taken from commercial cylinders, and gas analyses on a Bone and Wheeler apparatus showed them to be at least 99·5 per cent pure. All these gases were passed through a liquid air trap to remove moisture and carbon dioxide before entering the oil. The carbon dioxide was obtained from the solid by evaporation and freed from moisture by passage through a trap cooled to $-80°$ C. All gases were passed through a long coil immersed in the thermostat to bring them to the required temperature before entering the saturating vessel.

Presentation of Results

According to Henry's Law, the mass of gas dissolved by a given volume of liquid at a fixed temperature is directly proportional to the pressure P, *i.e.*,

$$\text{mass} = KP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or, if the mass of gas dissolved is expressed in ml of gas at N.T.P/ml liquid (S),

$$S = kP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Although gas solubility may be expressed in terms of the constants K or k, it is more usual to use either the Bunsen or Ostwald absorption coefficient.

The Bunsen Coefficient (α_v) is defined as the volume of gas at N.T.P. dissolved in unit volume of the liquid when the partial pressure of gas is 760 mm Hg.

The Ostwald Coefficient (γ) is effectively the ratio of the concentration of the gas in the solution to its concentration in the gas phase (gm. mol/unit vol). Alternatively, it may be regarded as expressing the volume of gas dissolved in unit volume of liquid, the volume of gas dissolved being measured, not at N.T.P., but at the experimental conditions of pressure and temperatures at which the liquid is saturated with the gas. It is this coefficient that is often the more useful in carrying out calculations on pump systems, etc., and for this reason, the following tables of results include values for both Bunsen and Oswald coefficients.

The relationships between k,α_v, and γ are briefly indicated below :—

From (5) $$\alpha_v = 760\,k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By definition $\gamma = S(760/P)(T/273{\cdot}2)$

and substituting in (5)

$$\gamma = 760kT/273{\cdot}2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and hence also $$\gamma = \alpha_v(T/273{\cdot}2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Experimental Results

The majority of measurements were carried out at 20° C, and these are summarized in Table I. Physical properties of the oils used are given in the Appendix.

In order not to complicate comparisons between oils of different molecular weights and viscosities, data on lubricating oils have been limited to a number of solvent extracted fractions from the same crude (oils A.1 to A.5). In this way, it was thought that differences in solubility characteristics between these oil fractions would be due mainly to differences in molecular weight rather than in the type of molecule present. For comparison with oil A.2, oil B of the same DTD 472B grade but of unknown composition was investigated. Data on a typical kerosine were required in connexion with its performance in pumps, while the two gasolines and *iso*-octanes were used so as to obtain a comparison with earlier calculations of gas solubility from vapour evolution results obtained during a study of the vapour lock problem. Tests with *iso*-octane and the 100-octane fuels provided comparative data on the solubility of gases in a pure hydrocarbon and in a complex mixture of hydrocarbons. Finally, the limited determinations on water were made in order to check the apparatus and method against standard data given in the International Critical Tables.

The values in the last column of Table I, the " calculated " values of α_v for air, refer to the figures obtained from the results for oxygen and

TABLE I

Solubility Coefficients of Atmospheric Gases in Oils and Fuels

Temperature, 20° C; partial pressure, 760 mm Hg		Carbon dioxide		Oxygen		Nitrogen		Air (dry and CO_2-free)		Air calcd (dry and CO_2-free)
Liquid	Viscosity at 100° F, cs	a_v	γ	a_v	γ	a_v	γ	a_v	γ	a_v
Oil A.1	615	0·853	0·915	0·124	0·133	0·0662	0·0711	0·0783	0·0840	0·0782
Oil A.2	268	0·861	0·924	0·126	0·135	0·0664	0·0713	0·0792	0·0850	0·0789
Oil A.3	181	0·887	0·952	0·129	0·139	0·0717	0·0770	0·0843	0·0926	0·0838
Oil A.4	80·3	0·911	0·978	0·137	0·147	0·0748	0·0803	0·0878	0·0942	0·0871
Oil A.5	34·9	0·966	1·037	0·145	0·155	0·0762	0·0818	0·0903	0·0969	0·0905
Oil B	260	0·850	0·912	0·120	0·129	0·0644	0·0691	0·0752	0·0807	0·0760
Kerosine		1·51	1·62	0·212	0·228	0·118	0·127	0·136	0·146	0·138
100-octane fuel C		—	—	—	—	—	—	0·243	0·261	—
100-octane fuel D		—	—	0·344	0·369	0·204	0·219	0·235	0·252	0·233
iso-Octane (2 : 2 : 4-trimethyl pentane)		—	—	0·351	0·377	0·211	0·226	0·240	0·258	0·240
Water		—	—	—	—	—	—	0·01858 0·01875	—	—

nitrogen by assuming Dalton's Law of Partial Pressures in conjunction with Henry's Law; the composition of air is taken as 20·9 per cent oxygen and 79·1 per cent nitrogen by volume. Since the agreement between calculated and observed solubilities is almost always within 1 per cent, it appears that the assumptions are justified. Further, the agreement confirms the estimated accuracy of 1 per cent or better quoted earlier.

To study the effect of temperature on the solubility coefficient, measurements were carried out on some oils over the temperature range 0° to 100° C. After saturation at the required temperature, the oil was always cooled to room temperature before determination of the gas content. The calculation of α_v thus requires the density of the oil at the saturating temperature relative to that at room temperature. Density determinations were therefore carried out at 0°, 20°, and 100° C by the normal density bottle method. Over this temperature range, the density was found to vary linearly with temperature.

The solubility coefficients of several gases in oils A.2 and A.5 at 0°, 20°, 60°, and 100° C are given in Table II, and those for kerosine in Table III.

TABLE II

Solubility Coefficients of Gases in Oils A.2 and A.5
Variation with Temperature

Temperature, ° C	0° α_v	0° γ	20° α_v	20° γ	60° α_v	60° γ	100° α_v	100° γ
Oil A.2								
Hydrogen	0·0421	0·0421	0·0465	0·0499	0·0526	0·0642	0·0590	0·0806
Carbon dioxide	1·115	1·115	0·861	0·924	0·572	0·697	0·420	0·574
Oxygen	0·135	0·135	0·126	0·135	0·119	0·145	0·118	0·161
Nitrogen	0·0632	0·0632	0·0664	0·0713	0·0738	0·0901	0·0739	0·100
Air (dry and CO_2-free)	0·0794	0·0794	0·0792	0·0850	0·0835	0·1015	0·0818	0·112
Air (calc) (dry and CO_2-free)	0·0782	—	0·0789	—	0·0830	—	0·0829	—
Oil A.5								
Hydrogen	0·0452	0·0452	0·0483	0·0518	0·0549	0·0669	0·0658	0·0899
Carbon dioxide	1·245	1·245	0·966	1·037	0·640	0·781	0·467	0·638
Oxygen	0·150	0·150	0·1445	0·155	0·135	0·164	0·130	0·178
Nitrogen	0·0773	0·0773	0·0762	0·0818	0·0785	0·0957	0·0818	0·1113
Air (dry and CO_2-free)	0·0920	0·0920	0·0903	0·0969	0·0919	0·1121	0·0926	0·1265
Air (calc) (dry and CO_2-free)	0·0920	—	0·0905	—	0·0903	—	0·0919	—

TABLE III

Solubility Coefficients of Gases in a Typical Kerosine
Variation with Temperature

Temperature, ° C	0° α_v	0° γ	20° α_v	20° γ
Carbon dioxide	2·00	2·00	1·51	1·62
Oxygen	0·220	0·220	0·212	0·2275
Nitrogen	0·116	0·116	0·1185	0·127
Air (dry and CO_2-free)	0·139	0·139	0·136	0·146
Air (calc) (dry and CO_2-free)	0·138	0·138	0·138	0·148

DISCUSSION OF RESULTS

Effect of Temperature

Carbon Dioxide. The solubility of this gas in the liquids examined, as expressed by both Bunsen and Ostwald coefficients, is much greater at

20° C than that of the permanent gases, but it decreases rapidly with increasing temperature, as shown in Fig 3 for oils A.2 and A.5.

Oxygen. With this gas, it was found that a sealed sample of saturated

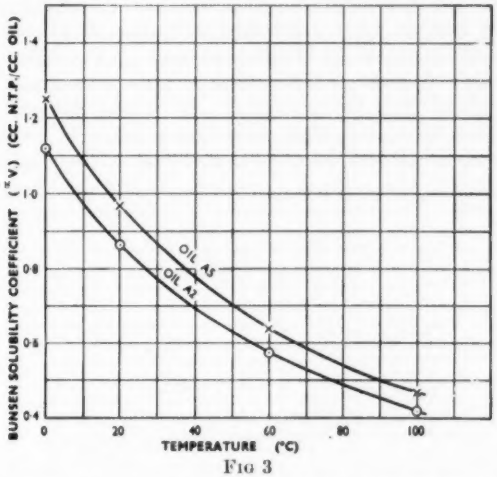

FIG 3

SOLUBILITY OF CARBON DIOXIDE IN OIL A.2 AND OIL A.5

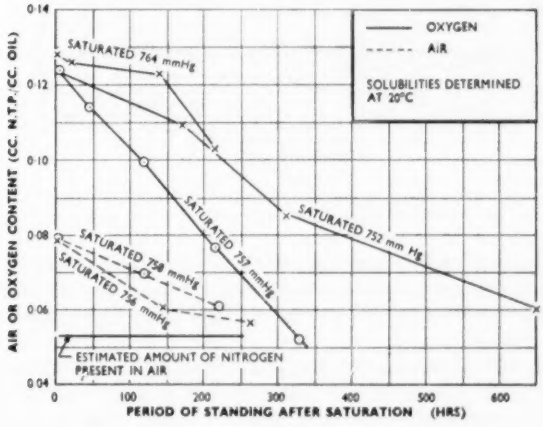

FIG 4

APPARENT CHANGE OF SOLUBILITY OF AIR AND OXYGEN IN OIL A.2 DURING STORAGE

oil yielded less gas when it had stood at atmospheric temperature for some days than it did immediately after saturation; further, the longer it stood the lower did the value become. Fig 4 shows typical curves illustrating the variation of oxygen content with time, from which it is evident that the results were not particularly repeatable. It appears from these results that

some slow chemical reaction occurs between some constituent of the oil and the dissolved oxygen, and that the rate of this reaction, estimated in terms of the amount of recoverable gas, may vary from sample to sample, although it was of the same order for all the lubricating oils examined. This phenomena has been noted by other workers.[11] As mentioned before, it was necessary to wait up to 1 hr after saturation was complete to allow bubbles in the oil to settle out before commencing a solubility determination. During this waiting period, some oxygen will react with the oil constituents and will not be recovered. By extrapolating the curves of Fig 4 back to zero time, it is clear that the amount of oxygen absorbed in this time is very small and the error introduced by the slight delay before

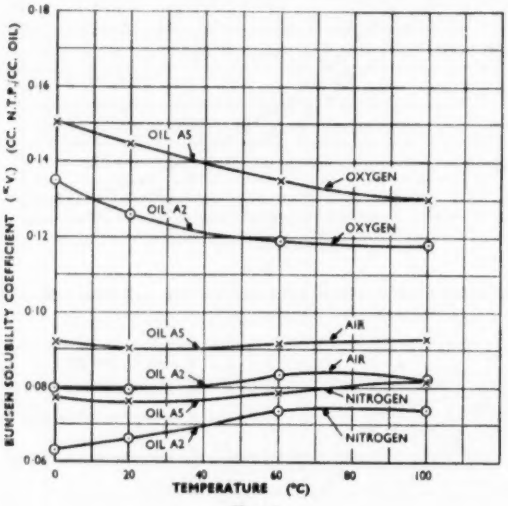

FIG 5

SOLUBILITY OF OXYGEN, AIR, AND NITROGEN IN OIL A.2 AND OIL A.5

measurement is less than 1 per cent for all oils investigated. The figures for the solubility of oxygen given in Tables I–III are those obtained from determinations carried out as soon as possible after the sample had been sealed off.

For the two oils examined the Bunsen coefficient decreases with increasing temperature by about 15 per cent over the range 0° to 100° C (Fig 5), but since the temperature coefficient of the Bunsen coefficient is less than the expansion coefficient of oxygen gas, the Ostwald coefficient increases by about 20 per cent over the same temperature range.

Nitrogen. The total variation of the Bunsen coefficient over the range 0° to 100° C is of the order of 17 per cent for oil A.2 and 8 per cent for oil A.5, the coefficient increasing with increasing temperature in the former case, though with oil A.5 there appears to be a slight minimum at about 20° C in the Bunsen coefficient–temperature curve (Fig 5). The Ostwald coefficient increases with increasing temperature (Table II).

There appears to be no indication of any reaction between nitrogen and the oil at room temperature; a saturated sample of oil A.5 had the same gas content (within experimental error) a week after saturating as it did an hour after saturating at 20° C. This observation also indicates that the oil samples are homogeneous with respect to the gas content.

Air. Since air is a mixture of some 20 per cent oxygen and 80 per cent nitrogen, its solubility in any liquid will be determined mainly by the solubility of nitrogen in that liquid, and to a lesser extent only by the solubility of oxygen. Since the Bunsen coefficient of oxygen decreases from 0° to 100° C, whereas that of nitrogen increases over the same range, the solubility of air in both oils A.2 and A.5 remains approximately constant, the total variation being only a few per cent (Fig 5).

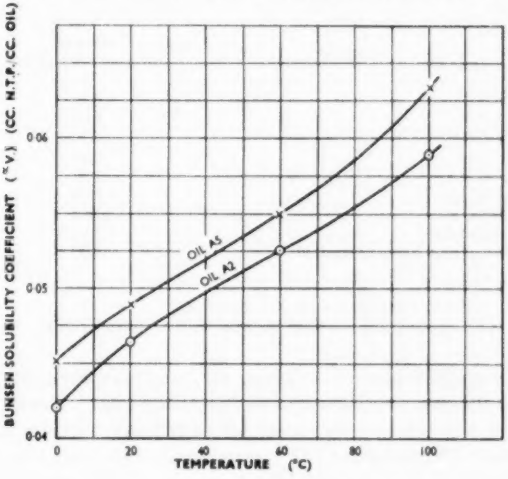

FIG 6

SOLUBILITY OF HYDROGEN IN OIL A.2 AND OIL A.5

As was observed with oxygen, the air content of a saturated sealed sample was found to decrease on standing, and this is illustrated in Fig 4. It would appear that the limiting value in this case is the solubility of nitrogen in the oil at its partial pressure in the atmosphere. This was confirmed by allowing a sealed sample of oil A.1, saturated at 20° C, to stand for six weeks. The gas content of the oil was then determined and found to be 0·061 cc gas at N.T.P. per cc oil, while the calculated value of nitrogen present in the oil when saturated is 0·0616 cc nitrogen at N.T.P. per cc oil.

As a result of the approximate constancy of the Bunsen coefficient, the Ostwald coefficient for air increases with increasing temperature for both oils.

Hydrogen. This gas is the least soluble of all those examined; both the Bunsen and Ostwald coefficients increase with increasing temperature, the former by some 50 per cent (Fig 6) and the latter by about 100 per cent over the range 0° to 100° C in oils A.2 and A.5.

The Effects of Viscosity and Molecular Weight

The viscosity of an undoped oil is largely a function of its molecular weight, so the effects of these two properties are closely related. Table I shows how the solubility decreases with increasing viscosity for the range of oils considered.

In order to ascertain whether any definite relationship between solubility and molecular weight exists for oils, the mean molecular weights of the liquids used were estimated to within about $\pm 5\%$ by the depression of the freezing point of naphthalene. The results obtained are shown in Table IV.

TABLE IV

Molecular Weights of Oils and Fuels Tested

Liquid	Mean molecular weight
Oil A.1	670
Oil A.2	610
Oil A.3	570
Oil A.4	530
Oil A.5	400
Oil B	630
Kerosine	165
iso-Octane	114 *
100-octane fuels C and D	100 †

* From formula—not determined.
† Estimated from density and mean boiling point.

In Fig 7 the solubilities of oxygen, air, and nitrogen in the oils are plotted against the mean molecular weights of the oils. It will be seen that the solubility of a given gas decreases fairly rapidly with increasing molecular weight from 100 to 400, after which the decrease is more gradual.

The solubilities of the atmospheric gases in oil B were determined in order to compare the results with the values obtained with oil A.2. These two oils are both of DTD 472B grade, but of different origin. The figures for the solubility in oil B are some 2 to 3 per cent lower than in oil A.2, and are lower even than the values for oil A.1, desite the higher molecular weight of the latter oil. It is evident that composition plays some part in determining solubility, but as the composition of oil B is not known, this factor cannot be further evaluated here.

The solubility of gases in pure *iso*-octane (2 : 2 : 4-trimethyl pentane) has been determined in order that the values for a pure hydrocarbon might be available. The values obtained for the two gasolines indicate that a small change in aromatic content has little influence upon the solubility of air.

As a check on the general reliability of the measurements, the solubility of air in water was determined. The experimental error was abnormally high here owing to the small pressures developed in the volume S as a result of the low solubility of air in this liquid, but the two values of the Bunsen coefficient obtained, 0·0186 and 0·0187(5), agree well with the values 0·01872 and 0·01868 given in the International Critical Tables.

Theoretical Discussion of Results

The above results were obtained primarily for purely practical discussions of problems in oil systems, and are far from being sufficiently complete for any theoretical treatment. Some interesting points emerge, however, when the results are examined in terms of current solubility theories.

Although the solubility of various gases has been determined in a wide variety of pure solvents, no theory has been developed which adequately covers the whole of the results obtained. Most workers have been content

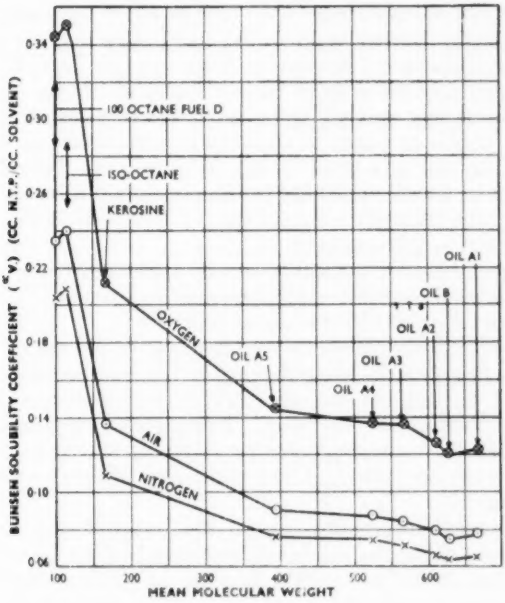

FIG 7

INFLUENCE OF MOLECULAR WEIGHT OF SOLVENT ON GAS SOLUBILITY AT 20° C

to develop semi-empirical expressions which relate only to the measurements they have made on a limited number of solvents and gases; a survey of these results has been made by Markham and Kobe.[1] The first simple and comprehensive attempt to interpret the figures for the solubility of gases in pure liquids was made by Hildebrand.[12] This theory was developed for pure liquids, but by assuming it to apply to mixtures also, it is possible to make some predictions about the solubility of gases in fuels and oils. For these reasons, the results will be discussed briefly from the view point of the Hildebrand theory.

The Solubility of Gases in Fuels and Oils on Hildebrand's Theory. By assuming Raoult's vapour pressure law to apply to a solution of a gas in a liquid, Hildebrand deduces the relation :—

$$S = P/P_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where S is the solubility of the gas in molar fractions;
P is the partial pressure of the gas above the solvent;
P_0 is the vapour pressure of the liquefied gas at the same temperature.

This expression can only be used to calculate the solubility of a gas at temperatures below the critical temperature of the gas, and so its application is somewhat limited, as the critical temperatures of most of the more common gases lie below 0° C. However, it is possible to extrapolate the vapour pressure curves at low temperatures of these gases up to room temperature, and so obtain an approximate value for the solubility.

The solubility of the gas obtained from equation (9) is usually termed the "ideal" solubility. Deviations from this ideal value may be expected with real gases, first, because of deviations from the gas laws, but more particularly through deviations from Raoult's law, which are to be expected when the solute and solvent differ in internal pressure and polarity. Bearing these points in mind, the following predictions can be made:—

1. For a given gas at a given partial pressure, the "ideal" solubility, expressed in molar fractions, should be the same in all solvents at any given temperature. The Bunsen coefficient should thus be inversely proportional to the molar volume of the solvent.

2. In practice, this ideal solubility will be approached only when the gas and solvent have similar internal pressures and polarity, and the more these differ, the lower will be the actual solubility.

3. Since the difference in solubility (in molar fractions) of a gas in two solvents arises largely from the difference in internal pressure and polarity of the solvents, the ratio of gas solubility in two solvents will be approximately constant for a series of gases. Exceptions to this must, of course, be expected if the two solvents differ very considerably in internal pressure polarity, and more particularly if one of the gases differs considerably from the other gases.

4. Since the vapour pressure P_0 of the liquefied gas increases with increasing temperature, the solubility, expressed either as molar fractions or as the Bunsen coefficient, should decrease as the temperature is raised. The effect may be counterbalanced, to some extent, by the increasing tendency to ideal behaviour as the temperature is raised.

5. Since P_0 is roughly determined by the critical temperature of the gas, the solubility of a gas should be greater, the higher its critical temperature.

The first of these predictions is examined in Table V. It will be seen that the solubilities quoted are of the same order as the "ideal" solubility, but that agreement is only sufficient for a rough estimate of solubility. In different solvents the solubility in molar fractions is approximately constant (particularly in view of the uncertainty attached to the molecular weight determinations, which enter into the conversion from the Bunsen coefficient to the solubility in molar fractions), but again significant variations are experienced.

The second prediction suggests that, since most of the common gases have low internal pressures and polarity, the solubility should be greater in paraffin hydrocarbons, which have lower internal pressures than aromatic hydrocarbons. This may account for the relatively low solubility figures for the kerosine (22 per cent aromatics, 53 per cent naphthenes).

The third prediction is examined in Table VI, which gives, for each liquid, the solubility relative to oil A.2 as unity for the four gases studied. The approximate constancy of the ratio, independent of the gas, will be

TABLE V

The Solubility of Gases in Molar Fraction at 20° C

Solvent	Carbon dioxide	Nitrogen	Oxygen	Hydrogen
Oil A.1	0·028	0·0022	0·0041	—
Oil A.2	0·026	0·0020	0·0039	0·0014
Oil A.3	0·025	0·0021	0·0037	—
Oil A.4	0·024	0·0020	0·0037	—
Oil A.5	0·019	0·0016	0·0029	0·0010
Oil B	0·026	0·0020	0·0038	—
Kerosine	0·014	0·0011	0·0019	—
iso-Octane	—	0·0016	0·0026	—
Ideal solubility	0·0177	0·0010	0·0013	0·0008

TABLE VI

Ratio of Solubility Coefficients in Various Solvents at 20° C

Liquid	Bunsen solubility coefficients relative to that for Oil A.2			
	Carbon dioxide	Oxygen	Hydrogen	Air
Oil A.1	0·991	0·984	0·997	0·989
Oil A.2	1·000	1·000	1·000	1·000
Oil A.3	1·030	1·024	1·080	1·064
Oil A.4	1·058	1·087	1·126	1·108
Oil A.5	1·122	1·151	1·147	1·140
Oil B	0·989	0·952	0·970	0·950
Kerosine	1·754	1·683	1·783	1·717
100 octane fuel D	—	2·730	3·072	2·967
iso-Octane	—	2·778	3·178	3·030

TABLE VII

Ratio of Solubilities for Gases in Oils A.2 and A.5

Gas	Ratio of Bunsen coefficients at temperature of :—			
	0° C	20° C	60° C	100° C
Carbon dioxide	1·12	1·12	1·12	1·11
Oxygen	1·09	1·14	1·14	1·10
Nitrogen	1·22	1·14	1·06	1·10
Air	1·16	1·14	1·10	1·13
Hydrogen	1·10	1·04	1·04	1·11

noted. Table VII gives similar data for the two oils A.2 and A.5 at various temperatures.

The ratio in Table VII remains remarkably constant, despite the wide variation in temperature and the thirty-fold variation in actual solubility

coefficients. The average ratio differs appreciably from the theoretical ratio of the molar volumes, which is about 1·58. This discrepancy may perhaps be partly due to errors in molecular weight determination, but in any case is to be expected as a consequence of the differing internal pressures and polarities of the two liquids. Prediction (3), therefore, forms a useful and reasonably accurate method of estimating solubility data for a number of gases in a given oil if the solubility of one gas is available, together with the necessary data for another oil.

The fourth prediction, decreasing solubility coefficient with increasing temperature, is confirmed in the cases of carbon dioxide and oxygen; with nitrogen the results are variable, while hydrogen shows an increasing solubility with increasing temperature. This may be attributed to the compensation resulting from increasing tendency to ideal behaviour as the temperature is raised.

The fifth prediction, the relation between solubility and critical temperature of the gas, is examined in Table VIII.

TABLE VIII

Relation between Gas Solubility and Critical Temperature

Gas	Critical temperature, °C	Solubility at 20° C at 1 atm in molar fractions	
		Oil A.2	Oil A.5
Hydrogen	−235	0·00143	0·00098
Nitrogen	−146	0·00204	0·00155
Oxygen	−119	0·00386	0·00293
Carbon dioxide	31	0·0258	0·0193

It will be seen that this relation enables some estimate of solubility to be made for an unknown gas, provided the internal pressure and polarity of the gas are not particularly high compared with those gases which are used for comparison.

It may be concluded, then, that the Hildebrand treatment gives a reasonable method of predicting trends in the solubility of gases in fuels and oils, particularly if allowances are made for the deviations from Raoult's Law resulting from the differences in internal pressure and polarity of the solute and solvent. Since the solvents used were mainly hydrocarbon mixtures, the molecules of which are mainly non-polar and symmetrical, it was thought that Raoult's Law would hold fairly closely. However, a few measurements were made of the depression of the vapour pressure of neo-hexane by the addition of oil. These indicated that at low oil concentrations Raoult's Law was fairly closely obeyed, the values of the molecular weight calculated from these vapour pressure depressions being in good agreement with those obtained by the freezing point method. At higher oil concentrations serious deviations from Raoult's Law were obtained, the apparent molecular weight being less than half that given by freezing point depression measurements. Since such deviations occur in the favourable case of neo-hexane–oil mixtures, deviations may also be expected with solutions of gases in oils and hydrocarbon mixtures. However, comparison with published results

shows that the deviations from Hildebrand's theory encountered with hydrocarbon mixtures are no greater than those encountered with pure liquid solvents. It may be concluded therefore, that oils and fuels, despite their complex nature, behave from the point of view of gas solubility in a very similar manner to pure liquids.

Other Theoretical Treatments. Uhlig [13] has developed a semi-empirical expression relating solubility to surface tension, and has shown this to hold for a number of solvents. His formula is :—

$$\log_e \gamma = E - 4\pi r^2 \sigma / kT \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where γ is the Ostwald solubility coefficient;
σ is the surface tension of the solvent;
E is the solute–solvent interaction energy;
r is the solute molecular radius;
T is the absolute temperature;
k is the Boltzmann constant.

Figs 8 and 9 show plots of $\log_{10} \gamma$ against σ for carbon dioxide, nitrogen, oxygen, and air in the solvents investigated. The results give a linear

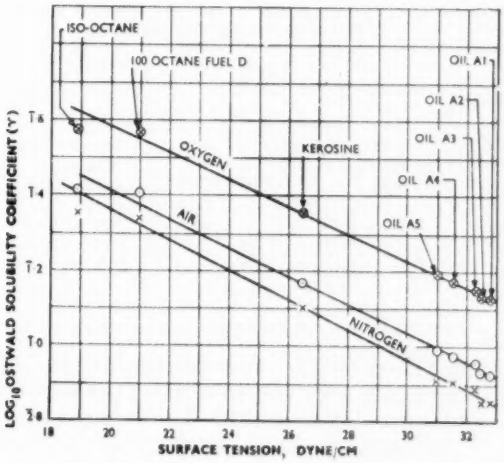

FIG 8

RELATION BETWEEN $\log_{10} \gamma$ AND SURFACE TENSION OF SOLVENTS. TEMPERATURE 20° C; PRESSURE 760 MM HG

plot, and the solute molecular radii, when calculated from the gradients of the straight lines, agree fairly well with those obtained by Uhlig, and with the values obtained by independent methods. These results are shown in Table IX, and for comparison purposes values deduced from gas viscosity measurements and van der Waals constants are included.

It is of interest to note that in the present work there appears no simple relationship between viscosity and solubility such as that put forward by Thorpe and Rogers.[14]

The most recent treatment of solubility involves the introduction of partition functions of the solute and solvent.[15] Owing to the complexity of the molecules present in oils, it is clear that these methods cannot easily be applied to solubility in oils and fuels.

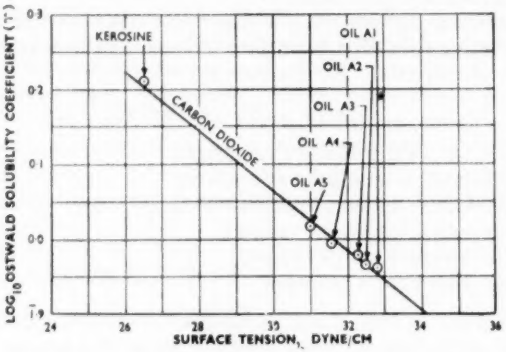

FIG 9

RELATION BETWEEN $\log_{10} \gamma$ AND SURFACE TENSION OF SOLVENTS. TEMPERATURE 20° C; PRESSURE 760 MM HG

TABLE IX

Gas	Molecular radius, cm			
	From Figs 11 and 12	Uhlig's values	Viscosity measurements	van der Waals constants
Carbon dioxide .	$1{\cdot}71 \times 10^{-8}$	—	$2{\cdot}14 \times 10^{-8}$	$1{\cdot}70 \times 10^{-8}$
Oxygen . .	$1{\cdot}63 \times 10^{-8}$	$1{\cdot}36 \times 10^{-8}$	$1{\cdot}70 \times 10^{-8}$	—
Nitrogen . .	$1{\cdot}71 \times 10^{-8}$	$1{\cdot}43 \times 10^{-8}$	$1{\cdot}75 \times 10^{-8}$	$1{\cdot}76 \times 10^{-8}$

CONCLUSIONS

The method described in this paper permits the determination of the solubilities of gases in oils and fuels to within 1 per cent or better, and is particularly suitable for viscous liquids. For a series of solvent extracted mineral oils of different viscosities derived from the same crude, the solubility decreases as the average molecular weight increases, but not according to any simple relation, and it is evident that the composition of the oil is also important. Owing to the number and complexity of the hydrocarbons which are present in oils and fuels, it is difficult to correlate the results of solubility measurements with those for pure liquids. However, it is evident that despite their complexity, they behave in a similar manner to pure liquids, and their deviations from current solubility theories are no more marked than those of many pure liquids.

ACKNOWLEDGMENT

The authors wish to thank the directors of The Shell Petroleum Co. Ltd. for permission to publish this paper.

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APPENDIX

(*a*) Properties of Oils

Oil	Sp Gr 15°/4° C	Flash point (closed), °F	Kinematic viscosity, cs		V.I.	Pour point, °F
			100° F	210° F		
A.1 (Residual) .	0·894	510	615	34·4	95	0
A.2 * (Residual) .	0·885	460	268	20·3	96	0
A.3 (Residual) .	0·884	440	181	15·7	97	5
A.4 (Distillate) .	0·873	445	80·3	9·1	96	0
A.5 (Distillate) .	0·869	350	34·9	5·4	96	0
B * . . .	0·890	460	260	20·0	96	10

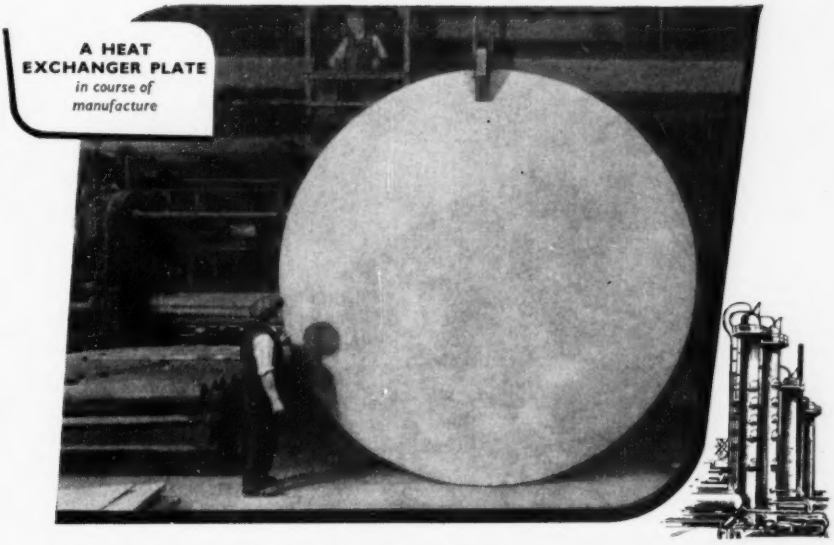
* Conforms to DTD 472B specification.

(*b*) Composition and Properties of Fuels

Fuel	Composition	Hydrocarbon analysis	T.E.L., ml/I.G.
Typical kerosine	Unknown	3% Olefins 22% Aromatics 53% Naphthenes 22% Paraffins	Nil
100-octane fuel C	40% Hydrocodimer 43% Hydro-base 3% Straight run 14% *iso*Pentane	2% Olefins 2–3% Aromatics 22% Naphthenes 73–74% Paraffins	4·0
100-octane fuel D	38·3% Alkylates 45·1% Straight run 13·5% *iso*Pentane 3·1% Benzole	1·5% Olefins 12% Aromatics 14% Naphthenes 72·5% Paraffins	4·8
iso-Octane (2.2.4 trimethyl pentane)	Pure compound	100% Paraffin	Nil

Fuel	Density 15°/4° C	Vapour pressure, Reid at 100° F p.s.i.	Vapour pressure, air-free at 20° C, mm Hg	ASTM distillation
Typical kerosine *	0·822	—	4	I.B.P. 137° C 10% rec. at 162·5° C 50% „ „ 196 90% „ „ 240 E.P. 264
100-octane fuel C	0·7096	6·8	184	I.B.P. 46° C 10% rec. at 62 50% „ „ 99 90% „ „ 117 E.P. 142
100-octane fuel D	0·7188	6·2	179	I.B.P. 43° C 10% rec. at 57 50% „ „ 91 90% „ „ 119 E.P. 164
iso-Octane (2.2.4 trimethyl pentane)	0·694	—	38	B.P. 99·24° C at 760 mm Hg (Freezing point −107·41° C)

* Kinematic viscosity 4·5 cs at 0° F, 2·75 cs at 32° F.



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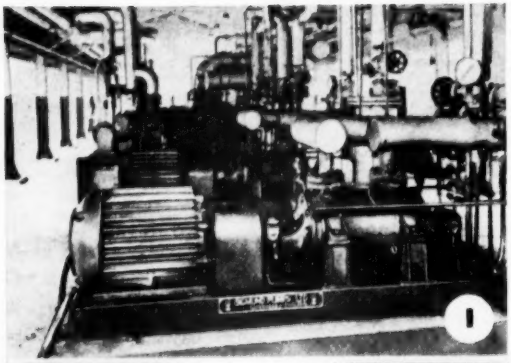

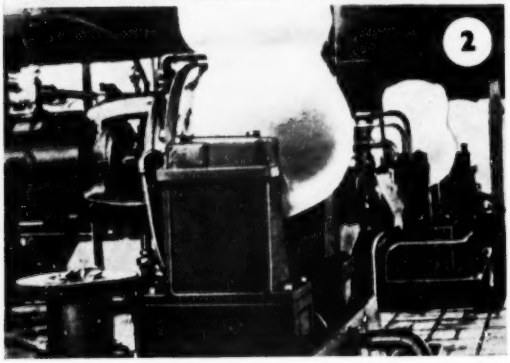

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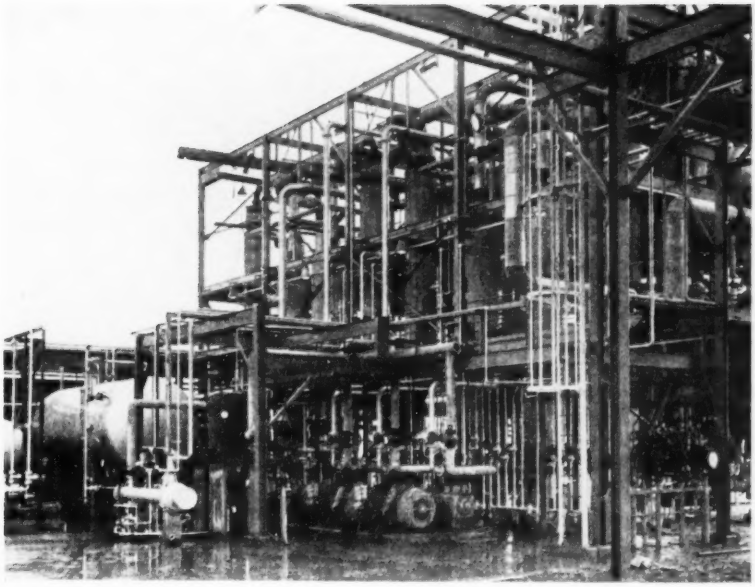

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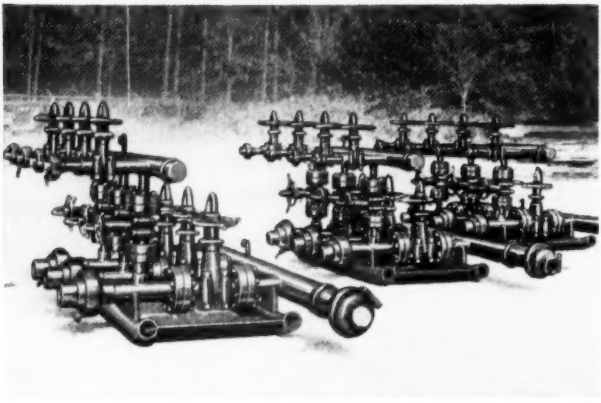

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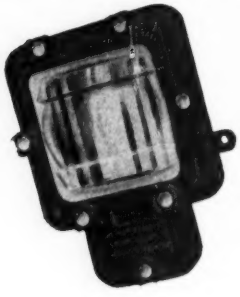

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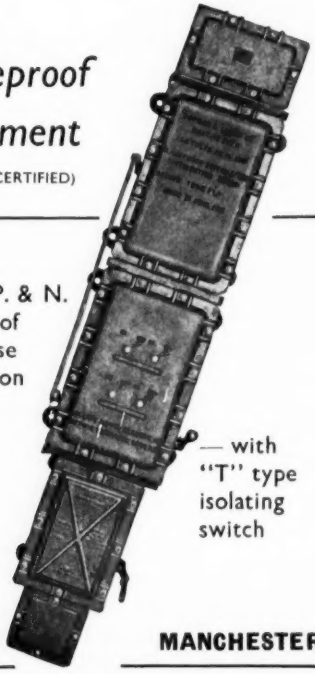

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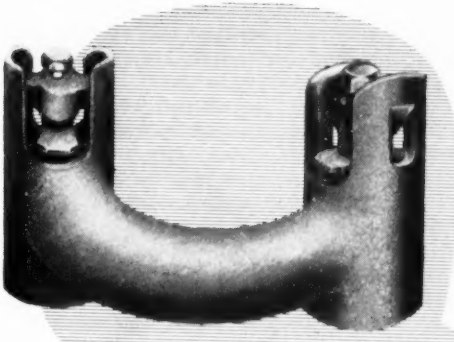

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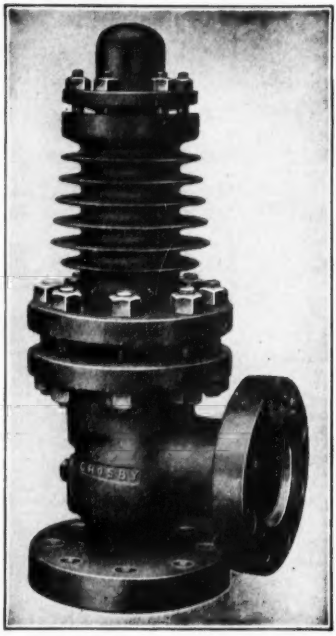

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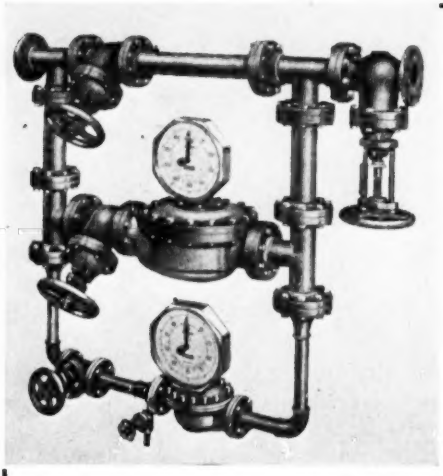

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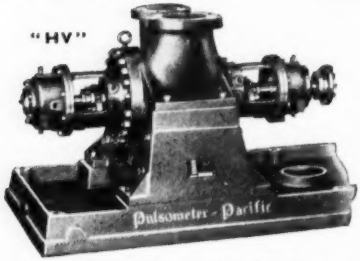

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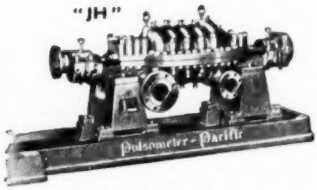

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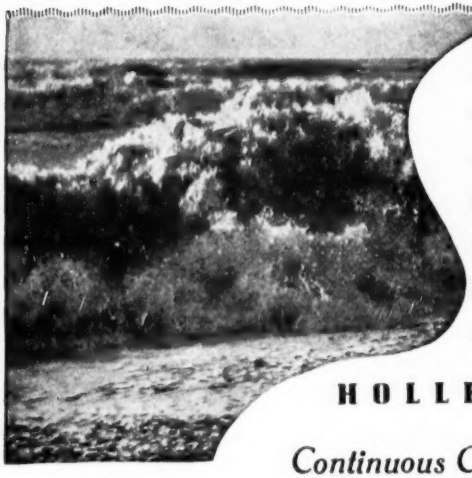

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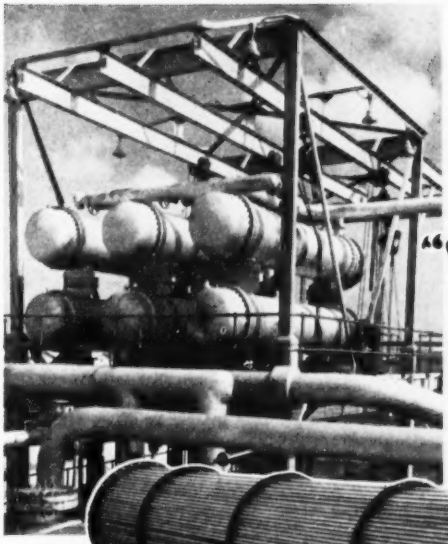

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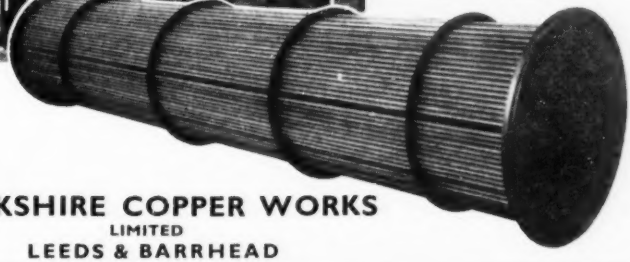

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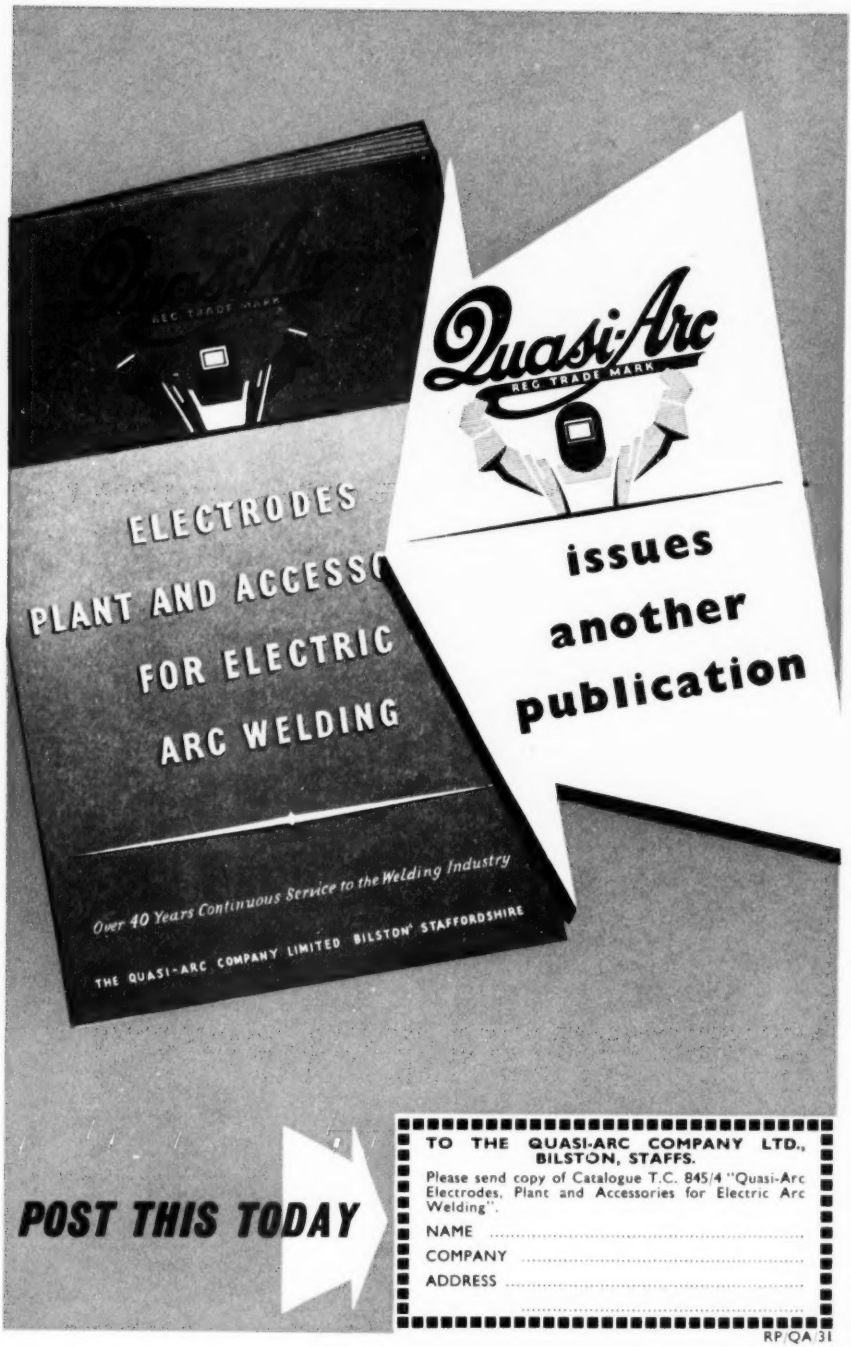
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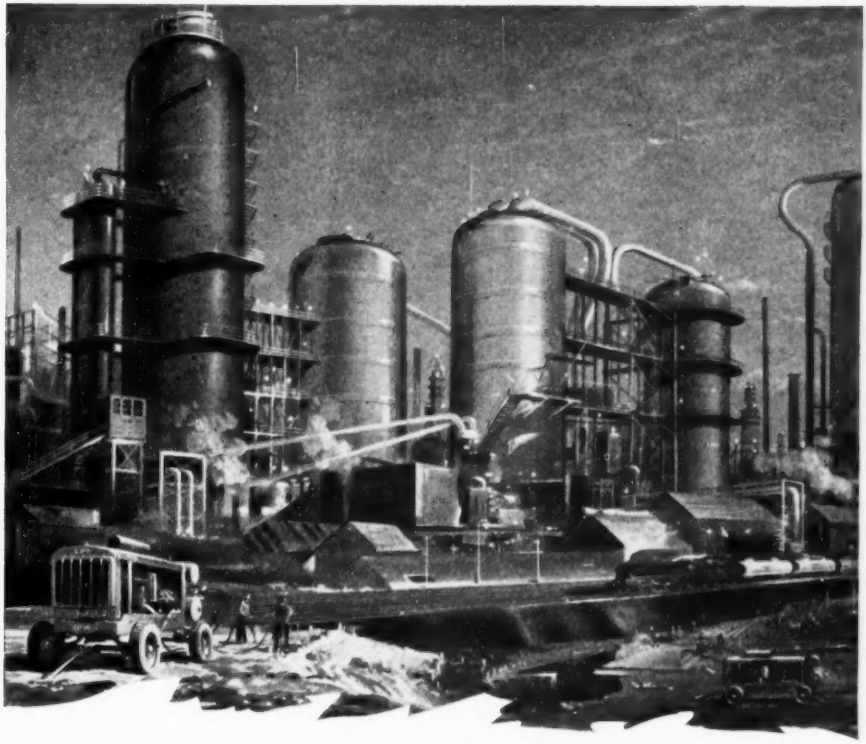

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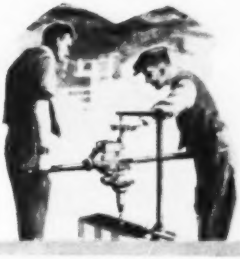

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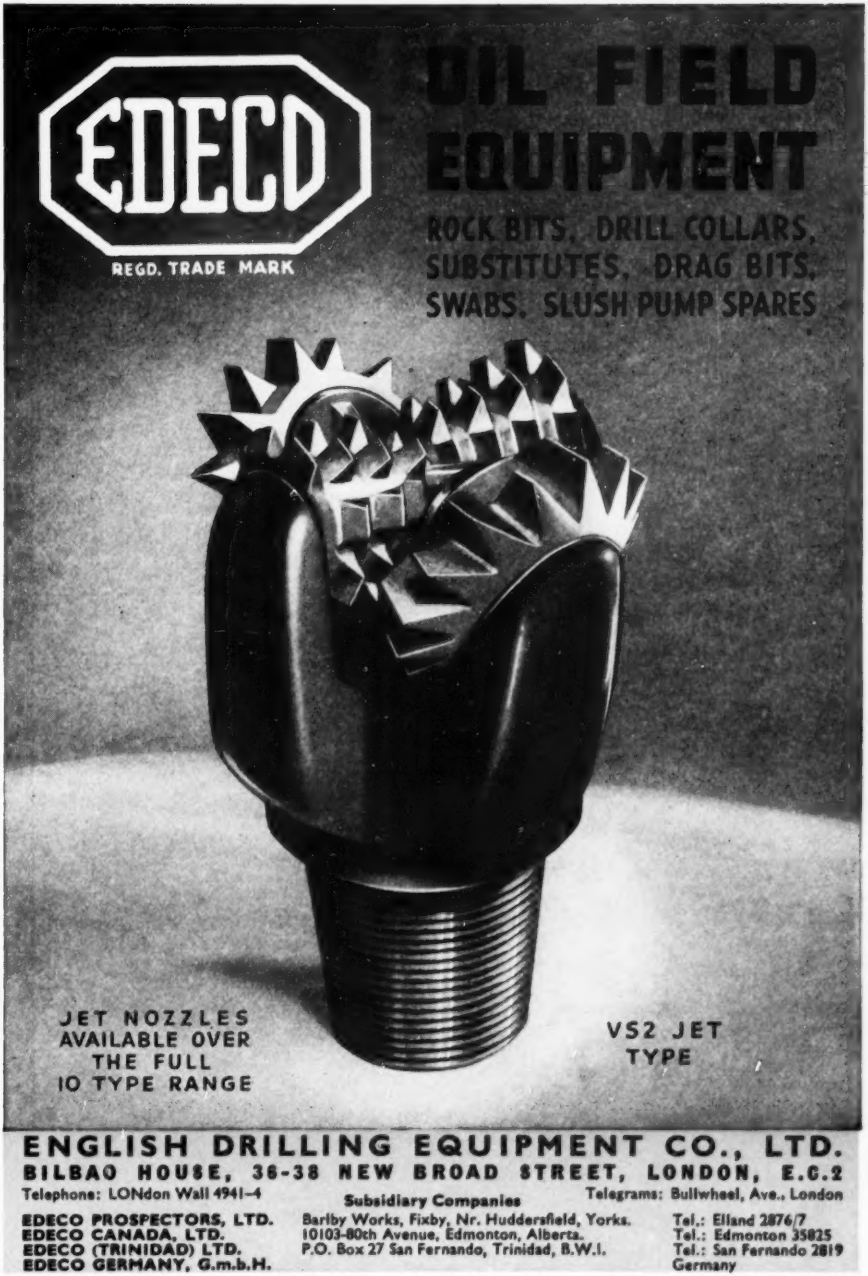
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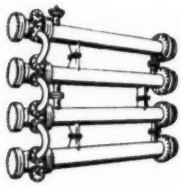

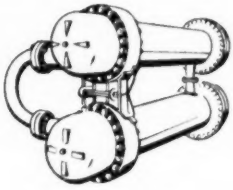

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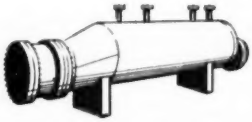

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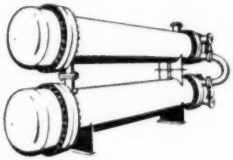

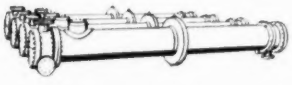

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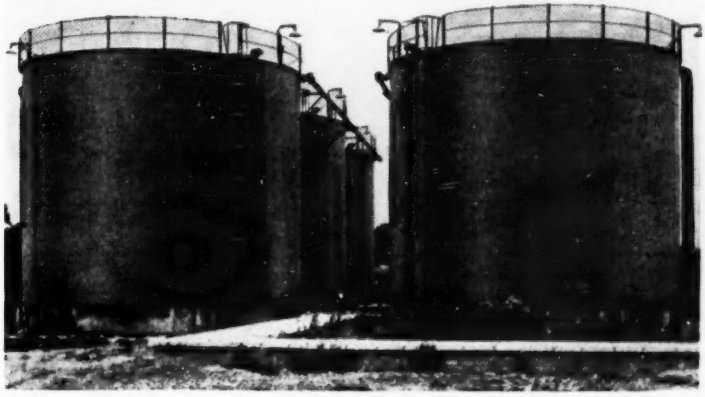

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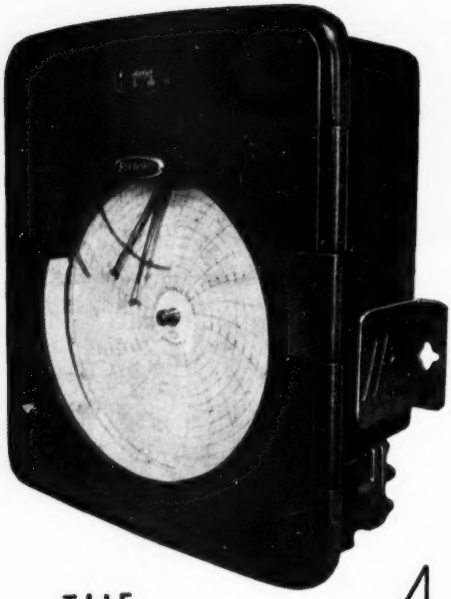

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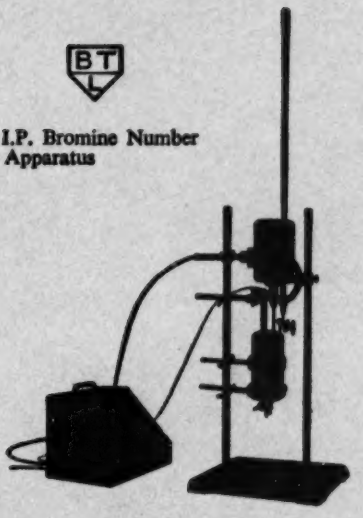

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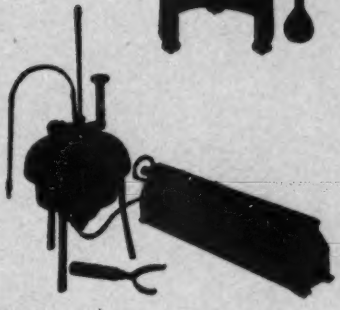

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